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COLLABORATIVE STUDY OF METHOD FOR THE DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE MONITORING SERIES

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Southwest Research Institute

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16. ABSTRACT

Statistical analyses are performed on data obtained in collaborative testing of EPA Method 8 (Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions From Stationary Sources) and from ancillary tests performed in conjunction with the analysis of the field samples. A collaborative test was conducted using four laboratory teams at a sulfuric acid plant. A total of 14 sampling runs were made, and a total of 52 determinations. Using these data, estimates are made of the precision that can be expected from a single team, and between two independent teams.

There was a tendency in these data for occasional high reported concentrations of sulfuric acid mist. On these samples, there was noticed a concurrent tendency for low reported sulfur dioxide concentrations. Since it cannot be determined that this phenomenon is unrelated to the method, these values are included in the data set to obtain the precision estimates. In addition, a second analysis is done with the six highest H_2SO_4/SO_3 values removed, and the improvement in the precision is noted.

Statistical analysis of the results of using the analytical part of the method on standard sulfate solutions provides estimates of the variability associated with this phase alone. These results are compared to the results from an earlier study on EPA Method 6 (Sulfur Dioxide) which uses the same barium-thorin titration procedure. Combined estimates for this analytical procedure are presented.

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COLLABORATIVE STUDY OF METHOD FOR THE DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

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SUMMARY AND CONCLUSIONS

This report presents the analyses of data which were obtained from collaborative testing of EPA Method 8 (Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources). Method 8 specifies that a gas sample be extracted from a sampling point in the stack and the acid mist including sulfur trioxide be separated from sulfur dioxide. Both fractions are then measured separately by the barium-thorin titration method.

The collaborative test was conducted at a sulfuric acid plant. The samples were collected by traversing the stack according to EPA Method 1, as specified in the test methods and procedures section of the *Federal Register*. Fourteen sampling runs were made, but one lab did not participate in the first two, and twice collaborators had to abort runs due to equipment difficulties. This resulted in a total of 52 separate determinations for each of sulfur dioxide and sulfuric acid mist.

Separate precision estimates are obtained for the determination of each pollutant. In addition, standard sulfate solutions were prepared for analysis by the collaborators in conjunction with the source samples. The actual concentration of these was unknown to the collaborators, so these allow an assessment to be made of the accuracy and precision of the analytical phase by itself.

There were several high values in the acid mist determinations which were of a magnitude to suggest that they were not representative of the true concentration in the stack. These values were associated with low sulfur dioxide concentrations at a higher frequency than could be expected from chance alone. The conclusion was that some condition existed which caused these values to occur together. Since it was impossible to determine that these were invalid determinations, the evaluation of Method 8 was performed with these in the data set. However, to allow for the possibility that this phenomenon is not method-related, the six acid mist values above 60 lb/scf $\times 10^{-7}$ were excluded, along with their corresponding sulfur dioxide values, and a separate evaluation performed. The results are summarized below.

Method 8—The precision estimates are given below in terms of between-laboratory, within-laboratory, and laboratory bias components.

(1) SO_2—The precision components for the sulfur dioxide data are shown to be independent of the mean level. The estimated between-laboratory standard deviation is 98.60 lb/scf $\times 10^{-7}$ with 3 degrees of freedom. The within-laboratory standard deviation is estimated as 76.94 lb/scf $\times 10^{-7}$ with 40 degrees of freedom. From these, a laboratory bias standard deviation of 61.66 lb/scf $\times 10^{-7}$ is estimated.

(2) H_2SO_4/SO_3—The precision components for the sulfuric acid mist data are shown to be proportional to the mean level, δ. The between-laboratory standard deviation is estimated as 95.8 percent of δ with 3 degrees of freedom. No within-laboratory or laboratory bias terms could be estimated due to the high values.

Method 8, High Values Excluded—The precision estimates follow the same models as in the full data sets.

(1) SO_2—The estimated between-laboratory standard deviation is 71.50 lb/scf $\times 10^{-7}$ with 3 degrees of freedom. The within-laboratory standard deviation is estimated as 76.94 lb/scf $\times 10^{-7}$ with 40 degrees of freedom. From these, a laboratory bias standard deviation of 61.66 lb/scf $\times 10^{-7}$ is estimated.

(2) H_2SO_4/SO_3—The estimated between-laboratory standard deviation is 66.1 percent of δ with 3 degrees of freedom. The estimated within-laboratory standard deviation is 58.5 percent of δ with 42 degrees of freedom. This gives an estimated laboratory bias standard deviation of 30.8 percent of δ.

Analytical Phase—The results from the analyses of the unknown sulfate solutions are used to evaluate the accuracy and precision of the analytical phase of the method separate from the field phase.

(1) **Precision.** The precision of the analytical phase of the method is expressed in terms of within-laboratory, between-laboratory and laboratory bias terms. The within-laboratory standard deviation is independent of the mean level and is estimated as 2.19×10^{-7} lb/scf. The between-laboratory standard deviation is proportional to the mean level and is estimated as 3.68 percent of δ. The laboratory bias standard deviation is estimated to be 3.53 percent of δ.

(2) **Accuracy.** The analytical phase is shown to be accurate, within the precision of the method, at all three levels of concentration studied. These levels cover the range from 158.6×10^{-7} to 669.8×10^{-7} lb/scf.

A comparison is made between the analytical phase results from this test and the results of a similar test performed in conjunction with collaborative testing of Method 6 (Sulfur Dioxide) which utilizes the same barium-thorin titration procedure for sample analysis.

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I. INTRODUCTION

This report describes the work performed and the results obtained on Contract 68-02-0626, Southwest Research Institute Project 01-3462-005, which includes collaborative testing of Method 8 for sulfur dioxide and sulfuric acid mist emissions as given in "Standards of Performance for New Stationary Sources."(3)*

This report describes the collaborative testing of Method 8 at a sulfuric acid plant, the statistical analyses of the data and the conclusions based on the analyses of the data.

*Superscript numbers refer to List of References at the end of this report.

II. COLLABORATIVE TESTING OF METHOD 8

A. Collaborative Test Site

Arrangements were made for a collaborative test of Method 8 at NL Industries Titanium Pigment Division sulfuric acid plant in St. Louis, Missouri.

The plant site was visited in August, 1973, to evaluate suitability for collaborative testing. The sulfuric acid plant is a sulfur burning unit, and utilizes a dual absorption process. Rated capacity of the unit is 900 tons/day of concentrated H_2SO_4. The exhaust gas from the absorbers is fed to a 200-ft-high stack. A 360-deg platform located on the stack 129 ft above grade was selected as the sample point. Diameter of the stack at the sample point is 6 ft. Sample ports were not available at this platform, and arrangements were made for the installation of four sample ports spaced 90-deg apart, located 5 feet above the platform floor. This placed the sample ports 41 ft above a constriction in the stack and 66 ft below the stack outlet. As a result, 20 traverse points were selected, 10 on each diameter. Due to the relatively small work space on the sampling platform, the control consoles were located on a platform 62 ft above grade, and 67 ft below the sampling platform. Arrangements were made to obtain plant analytical data on the stack gas, and to obtain daily sulfuric acid production data.

An overall view of the sampling site is shown in Figures 1 and 2. In Figure 1, both the sample platform and the platform on which the consoles were placed can be seen, while Figure 2 shows the sample platform. Typical velocity profiles in the stack are shown in Figure 3.

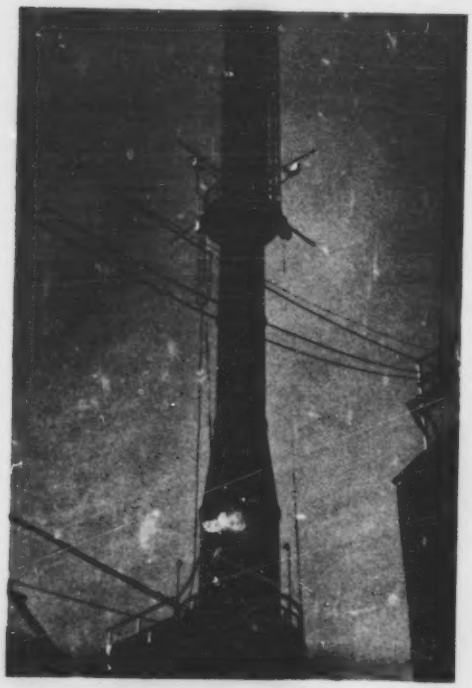

Figure 1. Overall View of Sampling Site

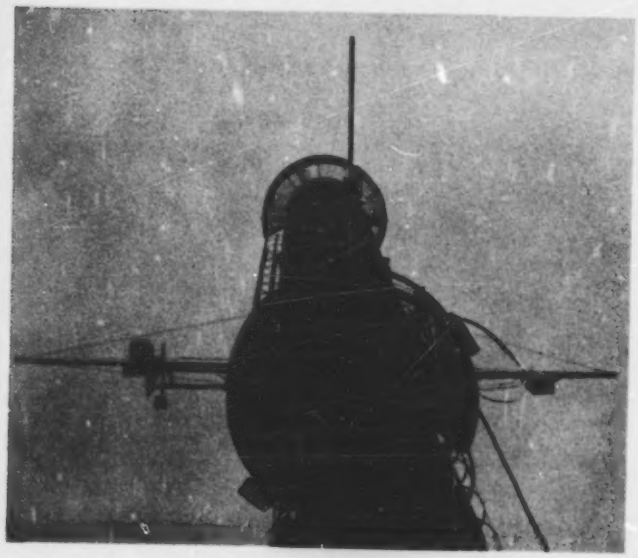

Figure 2. Sample Platform

B. Collaborators

The collaborators for the NL Industries sulfuric acid plant test were Mr. Charles Rodriguez and Mr. Ron Hawkins of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. Mike Taylor and

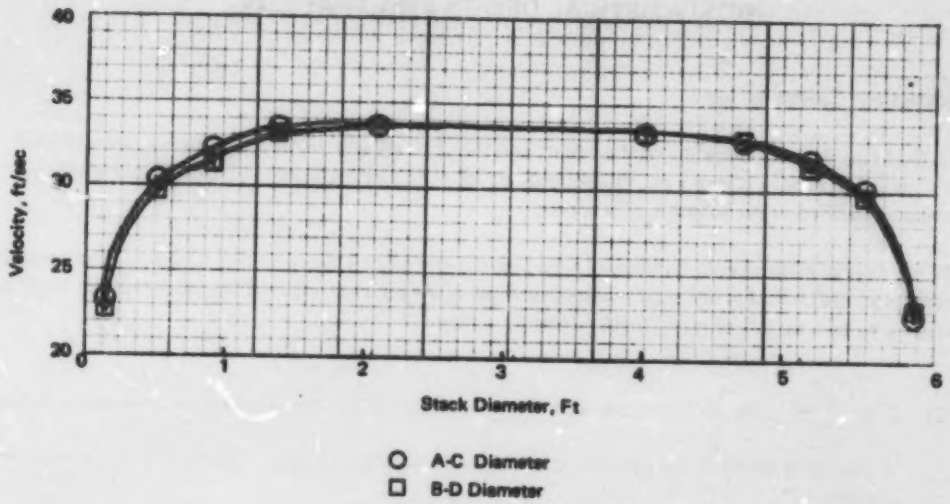

Figure 3. Typical Velocity Profile

Mr. Rick Hohman, Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. Roger Johnson and Mr. Bruce Callahan, Environmental Research Corporation, St. Paul, Minnesota; and Mr. Daniel Vornberg, Mr. Andrew Polcyn, Mr. David Givens, Mr. Richard Hagaman and Mr. J. W. MacClarence of Environmental Triple S, St. Louis, Missouri.

The collaborative test was conducted under the supervision of Mr. Nollie Swynnerton of Southwest Research Institute. Mr. Swynnerton had the overall responsibility for assuring that the test was conducted in accordance with the collaborative test plan and that the collaborators adhered to Method 8 as written in the *Federal Register.*(3) Collaborators for the test were selected by Dr. Henry Hamil of Southwest Research Institute.

C. Philosophy of Collaborative Testing

The concept of collaborative testing followed in the tests discussed in this report involves conducting the test in such a manner as to simulate "real world" testing as closely as possible. "Real world" testing implies that the results obtained during the test by each collaborator would be the same results obtainable if he were sampling alone, without outside supervision, and without any additional information from outside sources, i.e., test supervisor or other collaborators.

The function of the test supervisor in such a testing scheme is primarily to see that the method is adhered to as written and that no individual innovations are incorporated into the method by any collaborator. During the test program, the test supervisor observed the collaborators during sampling and sample recovery. If random experimental errors were observed, such as mismeasurement of volume of impinger solution, improper rinsing of probe, etc., no interference was made by the test supervisor. Since such random errors will occur in the everyday use of this method in the field, unduly restrictive supervision of the collaborative test would bias the method with respect to the performance test results which will be obtained when the method is put into general usage. However, if gross deviations were observed of such magnitude as to make it clear that the collaborator was not following the method as written, these would be pointed out to the collaborator and corrected by the test supervisor.

While most of the instructions in the *Federal Register* are quite explicit, some areas are subject to interpretation. Where this was the case, the individual collaborators were allowed to exercise their professional judgement as to the interpretation of the instructions.

III. STATISTICAL DESIGN AND ANALYSIS

A. Statistical Terminology

To facilitate the understanding of this report and the utilization of its findings, this section explains the statistical terms used in this report. The procedures for obtaining estimates of the pertinent values are developed and justified in the subsequent sections.

We say that an *estimator, $\hat{\theta}$, is unbiased for a parameter* θ if the expected value of $\hat{\theta}$ is θ, or expressed in notational form, $E(\hat{\theta}) = \theta$. From a population of method determinations made at the same true concentration, μ, let $x_1, \ldots, x_n$ be a sample of n replicates. Then we define:

(1) $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$ as the *sample mean,* an unbiased estimate of the *true determination mean,* δ, the center of the distribution of the determinations. For an accurate method, δ is equal to μ, the true concentration.

(2) $s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2$ as the *sample variance,* an unbiased estimate of the *true variance,* σ^2. This term gives a measure of the dispersion in the distribution of the determinations around δ.

(3) $s = \sqrt{s^2}$ as the sample standard deviation, an alternative measure of dispersion, which estimates σ, *the true standard deviation.*

The sample standard deviation, s, however, is not unbiased for σ,[2] so a *correction factor* needs to be applied. The correction factor for a sample of size n is α_n, and product of α_n and s is unbiased for σ. That is, $E(\alpha_n s) = \sigma$. As n increases, the value of α_n decreases, going for example from $\alpha_3 = 1.1284$, $\alpha_4 = 1.0854$ to $\alpha_{10} = 1.0281$. The formula for α_n is given in Appendix B.7.

We define

$$\beta = \frac{\sigma}{\delta}$$

as the *true coefficient of variation* for a given distribution. To estimate this parameter, we use a *sample coefficient of variation,* $\hat{\beta}$. defined by

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

where $\hat{\beta}$ is the ratio of the unbiased estimates of σ and δ. The coefficient of variation measures the percentage scatter in the observations about the mean and thus is a readily understandable way to express the precision of the observations.

There were a total of 14 sampling *runs* for the test. Since the actual sulfur dioxide and acid mist concentrations fluctuate, one can in general expect different true levels for each run. To permit a complete statistical analysis, the individual runs are grouped into *blocks,* where each block has approximately the same true concentration.

We can apply the statistical terms of the preceding paragraphs both to the collaborators' values during a given run and to each collaborator's values in a given block. In this report, statistical results from the first situation are referred to as *run results.* Those from the second situation are referred to as *collaborator-block results.*

For example, a run mean is the average of all the determinations made in a run as obtained by Method 8. A collaborator-block coefficient of variation is the ratio of the unbiased standard deviation to the sample mean for all the collaborator's runs grouped in the block.

The variability associated with a Method 8 determination is estimated in terms of the *within-laboratory* and the *between-laboratory precision components.* In addition, a *laboratory bias component* can be estimated. The following definitions of these terms are given with respect to a *true concentration,* μ.

- *Within-laboratory*—The within-laboratory standard deviation, σ, measures the *dispersion in replicate single determinations* made using Method 8 by one laboratory team (same field operators, laboratory analysts, and equipment) sampling the same true level, μ. The value of σ is estimated from within each collaborator-block combination.

- *Between-laboratory*—The between-laboratory standard deviation, σ_b, measures the *total variability in a determination* due to simultaneous Method 8 determinations by different laboratories sampling the same true stack concentration, μ. The between laboratory variance, σ_b^2, may be expressed as

$$\sigma_b^2 = \sigma_L^2 + \sigma^2$$

  and consists of a within-laboratory variance plus a *laboratory bias variance,* σ_L^2. The between-laboratory standard deviation is estimated using the run results.

- *Laboratory bias*—The laboratory bias standard deviation, $\sigma_L = \sqrt{\sigma_b^2 - \sigma^2}$, is that portion of the total variability that can be ascribed to differences in the field operators, analysts and instrumentation, and due to different manners of performance of procedural details left unspecified in the method. This term measures that part of the total variability in a determination which results from the use of the method by different laboratories, as well as from modifications in usage by a single laboratory over a period of time. The laboratory bias standard deviation is estimated from the within- and between-laboratory estimates previously obtained.

B. The Design and Conduct of the Collaborative Test

The collaborative test plan called for 16 sampling runs over a two-week period from October 22 to November 2, 1973. Only 14 runs were actually made because the unit was down for repairs during two days of the sampling period. Each sampling run was 2 hours in duration, with each team sampling 30 minutes at each of the four ports on the stack. The sampling sequence used by each collaborator to obtain the sample is shown in Table 1.

The starting port for each collaborator at the beginning of each day was chosen through a randomization technique, as was the direction of rotation to the next port. When a second run was made on a given day, the starting port was the finishing port of the first run, and the rotation was in the opposite direction. This was done to avoid entanglement of the umbilicals and to make the operation of the crews on the sampling platform easier.

In addition to the Method 8 samples, the collaborators were given three sulfate solutions to analyze in conjunction with the test samples. The concentrations of these solutions were unknown to the collaborators, and the analytical results allow estimation of the accuracy and precision of the analytical phase of the method. The collaborators were instructed to analyze each solution in triplicate on three separate days. These analyses were to be performed during the time period in which the stack samples were being analyzed. A copy of the instruction and data sheet given to the collaborators is shown in Figure 4.

During the course of the test, two operating parameters were observed for later use in estimating the true concentration level of the pollutants. The first was the Reich test for SO_2 in the gas stream, and the second was the daily amount of acid produced. The Reich test analyzes the exit gas for SO_2 and is made at 2-hr intervals

A series of sulfate solutions are provided to each collaborator. These solutions are labeled A, B, and C, and the concentrations are unknown to the collaborators.

Each unknown solution is to be analyzed in triplicate on each of three separate days during the period when analyses of the collaborators stack gas samples are being performed. Use a 10 ml aliquot, add 40 ml isopropanol and 2 to 4 drops Thorin indicator. Titrate the solution with 0.01N barium perchlorate to a pink endpoint.

Calculate the concentration in lbs/ft^3 using the following equation:

$$C_{SO_2} = \left(7.05 \times 10^{-5} \ \frac{\text{lb.-l.}}{\text{g.-ml}}\right) \frac{(V_t - V_{tb})(N)\left(\frac{V_{soln}}{Va}\right)}{V_{m_{std}}}$$

Use $V_{m_{std}} = 40\,ft^3$, $V_{soln} = 1000\,ml$, $V_a = 10\,ml$

Submit the results on this sheet along with your other collaborative test data.

Analyst:_____

		SO_2 Concentration, lb/ft^3		
Day	Replicate	Solution A	Solution B	Solution C
Day 1 Date_____	1			
	2			
	3			
Day 2 Date_____	1			
	2			
	3			
Day 3 Date_____	1			
	2			
	3			

Figure 4. Analysis of Unknown Sulfate Solutions

Table 1. Design of the Method 8 Collaborative Test

Day	Run	Port Sampling Sequence*			
		Lab 101	Lab 102	Lab 103	Lab 104
10/22/73	1	BCDA	–	CDAB	ABCD
10/23/73	2	ABCD	–	BCDA	CBAD
	3	DCBA	CBAD	ADCB	BADC
10/24/73	4	DABC	CDAB	BCDA	ABCD
	5	CBAD	BADC	ADCB	DCBA
10/29/73	6	DABC	ABCD	CDAB	BCDA
	7	CBAD	DCBA	BADC	ADCB
10/30/73	8	BCDA	CDAB	ABCD	DABC
	9	ADCB	BADC	DCBA	CBAD
10/31/73	10	DCBA	CBAD	BADC	ADCB
11/1/73	11	DABC	CDAB	BCDA	ABCD
	12	CBAD	BADC	ADCB	DCBA
11/2/73	13	CDAB	BCDA	ABCD	DABC
	14	BADC	ADCB	DCBA	CBAD

*Sequence BCDA means that consecutive radius traverse samples were obtained through port B, port C, port D, and port A.

during the day by plant personnel. The daily amount of acid produced is given as daily production rate in tons of 100 percent H_2SO_4/24 hr, proportional to the 10 hr of actual production.

One modification to the SO_2 sample recovery and analysis was found to be necessary. If the procedure specified in the method was used, excessively large volumes of titrant (greater than 50 mℓ) were required. To avoid the errors inherent in repeated filling of the burette during titration of a sample, the dilution factor during sample recovery was increased, and the aliquot size was decreased. The special instructions given the collaborators are shown in Figure 5.

C. Test Data

The determinations of sulfur dioxide and acid mist concentrations as reported by the collaborators are shown in Table B.1. The raw data sheets were provided to SwRI, and these were used to check the calculations of the collaborators. In this manner, the results reported here are not influenced by calculation errors. The recalculated values for the sulfur dioxide concentrations appear in Table 2 and the recalculated acid mist concentrations are in Table 3. A detailed discussion of the preliminary data analysis is in Appendix B.1.

SPECIAL NOTE TO COLLABORATORS

To avoid excessively large titrant volumes in the determination of SO_2 concentration (paragraph 4.3.1 and equation 8-3, Method 8, *Federal Register*, Vol. 36, Dec. 23, 1971) the following modification of Method 8 has been made for this test, with the approval of the EPA Project Officer.

Take the container holding the contents of the second and third impingers and add the contents to a one liter volumetric flask. Rinse the container with deionized distilled water and add the rinsings to the volumetric flask. Dilute to the mark with deionized distilled water. Mix thoroughly. Pipette a 10 mℓ aliquot of sample into a 250 mℓ Erlenmeyer flask. Add 40 mℓ of isopropanol and 2 to 4 drops of thorin indicator. Titrate with barium perchlorate to a pink endpoint. Record the volume of titrant. Repeat the titration with a second aliquot of sample. Titrate the blanks in the same manner as the samples.

It should be noted that this modification applies only to that portion of paragraph 4.3.1 concerning determination of SO_2 concentration. The initial portion of paragraph 4.3.1 concerning the determination of sulfuric acid mist remains unchanged, and should be followed as written in the *Federal Register*.

Figure 5. Special Instructions

There are four missing values in the data set. On the first day of testing, Lab 102 was not prepared to sample and missed both runs 1 and 2. On run 3, Lab 102 was forced to abort due to a broken carriage. On

run 6, Lab 104 could not complete the run due to broken glassware. There was no substitution made for these values, but rather the analysis was performed using only the 52 valid determinations.

There are some values in the data sets which appear unusual. In the acid mist concentration determination, there are values which range from 2 to 10 times the other values for that run. In the sulfur dioxide data, there are values which are on the order of one-half of the remaining values for that lab. While these would appear to be outliers in a statistical sense, they are not excluded from the analysis. Since there is no evidence to suggest that these determinations were made improperly, nor to indicate that this type of result is unexpected with the field use of Method 8, they are retained.

The interesting phenomenon is that the high mist and low sulfur dioxide determinations appear to occur in conjunction with one another. That is, a high acid mist concentration is usually accompanied by a low sulfur dioxide concentration. To investigate this idea, a correlation coefficient is determined between the SO_2 and H_2SO_4/SO_3 determinations. The details appear in Appendix B.2.

The correlation coefficient obtained from the 52 pairs of determinations is $r = -0.51$ which indicates a significant negative correlation. By investigating the correlation between determinations for each collaborator separately, it is apparent that this negative correlation is related to the occurrence of high acid mist determinations. The more high values in a lab's data, the greater the degree of correlation present. If the 6 values which exceed 60 lb/scf $\times 10^{-7}$* are deleted, the correlation among the remaining 46 pairs is estimated by $r = -0.14$, which is not significantly different from zero.

The conclusion drawn from this is that there is a reason for these values occurring together. What cannot be determined is whether the reason is related to Method 8 itself, or whether there was some disturbance or condition at the test site which led to this phenomenon. Without a strong basis, the values may not be removed

Table 2. Corrected Sulfur Dioxide Concentration Determinations Arranged by Block (lb/scf × 10^{-7})

Block	Run	Labs			
		101	102	103	104
1	4	313	403	298	284
	5	375	271	341	400
	10	461	436	327	242
2	1	453	*	226	506
	2	314	*	455	578
	3	401	†	367	233
	6	404	494	377	†
	7	412	564	166	491
3	8	428	562	402	438
	9	476	599	444	564
	11	301	587	432	514
	12	460	597	441	552
	13	483	579	459	379
	14	471	568	438	582

*Run not made.
†Run not completed due to glassware breakage.

Table 3. Corrected Acid Mist Concentration Determinations (lb/scf × 10^{-7})

Run	Labs			
	101	102	103	104
1	37.0	*	64.3	6.0
2	109.5	*	31.9	10.5
3	49.9	†	11.7	7.1
4	44.6	5.0	24.2	4.2
5	8.5	5.3	10.1	12.4
6	7.8	5.5	14.1	†
7	3.2	6.7	112.9	7.0
8	9.7	8.6	11.1	22.2
9	11.4	8.3	13.9	7.5
10	13.3	8.6	8.6	112.9
11	97.1	6.3	8.6	18.9
12	74.7	5.7	9.3	25.8
13	7.7	10.2	12.7	22.8
14	6.2	6.6	7.0	22.9

*Run not made.
†Run not completed due to glassware breakage.

*EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular nonmetric units used in the document. For this report, the factor is:

$$10^{-7} \text{ lb/scf} = 1.6018 \times 10^{3} \ \mu g/m^3.$$

from the data set prior to analysis. Thus, the results presented here for the method will be those obtained using all 52 concentration determinations for each pollutant. To account for the possibility that these values are not representative of a Method 8 test result, a second analysis is done on the data sets with high mist determinations and their corresponding sulfur dioxide values eliminated.

Since no techniques were available for producing a stable $SO_2/SO_3/H_2SO_4$/air mixture, there could be no assessment of the accuracy of the method. The statistical results contained in this report for the method concern only the precision that can be expected with its use as a field testing method.

The first step in the analysis is to group the runs into blocks. In Appendix B.3, the Friedman test is used to establish that the true mean concentration of sulfur dioxide varied over the test period. To account for this variation, three blocks are established based upon the operating parameters observed. The average values of the Reich test over each sampling run and the daily production rates are shown in Table 4. The first block consists of those runs where the Reich test was low (2.5), the second where the Reich was high and production rate was low, and the third where both were high. The run where the Reich test was not made was included in the third block on the basis of the high production rate. In Appendix B.3, the adequacy of this blocking scheme is demonstrated.

Table 4. Plant Operating Parameters During Sampling

Run	Reich Test, % SO_2	Daily Production Rate, tons H_2SO_4
1	3.0	915
2	3.0	913
3	3.0	913
4	2.5	915
5	2.5	915
6	3.0	919
7	3.0	919
8	*	940
9	3.0	940
10	2.5	923
11	3.0	949
12	3.0	949
13	3.0	947
14	3.0	947

SO_2 Blocking Scheme

Block	Runs
1	4, 5, 10
2	1, 2, 3, 6, 7
3	8, 9, 11, 12, 13, 14

*Not taken.

For the acid mist determination, the Friedman test indicates no significant variation in the true value from run to run. Thus, these runs are treated as a single block of size 14. The details of the Friedman test are shown in Appendix B.3.

The within-laboratory precision estimates are obtained from the collaborator-blocks under the assumption that each run in the block had the same true mean concentration. Since there is undoubtedly some variation in the concentration levels, it is likely that these estimates are conservative. That is, one would expect the within-laboratory variance, σ^2, to be no larger than the estimated value, and probably to be smaller.

The between-laboratory precision estimates are taken from the differences among laboratories in a sample run. As such, they represent differences between samples taken from the same traverse points during the same 2-hr period. The only possible fluctuation in the true concentration would be due to a changing pattern of gas flow during the course of the run.

IV. PRECISION ESTIMATES FOR METHOD 8

A. SO_2

Prior to analyzing the data, transformations are used to determine the distributional nature of the determinations. Three forms of the data are tested: linear, logarithmic and square root. The transformed data are tested using Bartlett's test for homogeneity of variance. The results of the transformations and tests are shown in Appendix B.4.

The original or linear form of the data obtains the highest degree of equality for the SO_2 data. The acceptance of the linear transform as the best model implies that there is a constant variance for both the run data and the collaborator-block data, regardless of the level of the mean concentration. These variances are estimated by combining the estimates obtained for them from each run and from each collaborator-block. The technique is referred to as pooling, and is discussed in Appendix B.4.

The precision estimates are of the form

$$s_p^2 = \frac{\sum_{i=1}^{k} (n_i - 1)s_i^2}{\sum_{i=1}^{k} (n_i - 1)}$$

where

s_i^2 – sample variance of the i^{th} sample

n_i – size of the i^{th} sample

k – number of samples

In Appendix B.5, the individual standard deviations and sample sizes are presented and used to obtain the precision estimates. The within-laboratory variance, σ^2, is estimated from the collaborator-block terms, and has an estimated variance, $\hat{\sigma}^2$, of

$$\hat{\sigma}^2 = 5920.12$$

with 40 degrees of freedom. The estimated within-laboratory standard deviation, then, is

$$\hat{\sigma} = \sqrt{5920.12}$$

$$= 76.94 \text{ lb/scf} \times 10^{-7}$$

Letting $\hat{\delta}$ represent the sample mean of all 52 determinations, it is possible to estimate a within-laboratory coefficient of variation as

$$\hat{\beta} = \frac{\hat{\sigma}}{\hat{\delta}}$$

$$= \frac{76.94}{429.77}$$

$$= 0.18.$$

The between-laboratory variance, σ_b^2, is estimated using the 14 run standard deviations obtained. Substituting into the pooled variance formula gives

$$\delta_b^2 = 9721.76$$

with 3 degrees of freedom. This gives an estimated between-laboratory standard deviation of

$$\delta_b = \sqrt{9721.76}$$

$$= 98.60 \text{ lb/scf} \times 10^{-7}$$

The between-laboratory coefficient of variation is

$$\hat{\beta}_b = \frac{\delta_b}{\bar{\delta}}$$

$$= \frac{98.60}{429.77}$$

$$= 0.23.$$

The laboratory bias variance, σ_L^2, is estimated from the above as

$$\delta_L^2 = \delta_b^2 - \delta^2$$

$$= (9721.76) - (5920.12)$$

$$= 3801.64,$$

with a laboratory bias standard deviation of

$$\delta_L = \sqrt{3801.64}$$

$$= 61.66 \text{ lb/scf} \times 10^{-7}$$

The laboratory bias coefficient of variation, then, is estimated by

$$\hat{\beta}_L = \frac{\delta_L}{\bar{\delta}}$$

$$= \frac{61.66}{429.77}$$

$$= 0.14.$$

B. H_2SO_4/SO_3

The acid mist determinations were passed through the same transformations as were the SO_2. In Appendix B.6, it is demonstrated that for these data, the logarithmic transformations gives the highest degree of equality of variance. This implies that there is a proportional relationship between the true mean and true standard deviation. That is, the variability in an acid mist determination increases as the mean concentration increases, but the ratio of the standard deviation to the mean, the coefficient of variation, remains constant. Thus,

$$\beta_b = \frac{\sigma_b}{\delta}$$

and

$$\beta = \frac{\sigma}{\delta}$$

provide the best information concerning the variability in the determination of acid mist concentration in a gas stream. To estimate the precision, then, the coefficients of variation are estimated and the standard deviations presented as a coefficient of variation times an unknown mean, δ.

In Appendices B.7 and B.8, the technique for obtaining a point estimate of a coefficient of variation from several individual estimates is presented. The run and block sizes vary since there are missing values in the data set, so the individual estimates are weighted according to their sample size.

For the run data, there are 14 individual estimates of β_b. In Appendix B.9, the estimates and their respective weights are shown. Combining these gives an estimated coefficient of variation, $\hat{\beta}_b$, of

$$\hat{\beta}_b = 0.958.$$

The standard deviation estimate, then, is

$$\delta_b = (0.958)\delta$$

or 95.8 percent of the mean value, with 3 degrees of freedom.

The collaborator-blocks give 4 estimates of β, the within-laboratory coefficient of variation. These estimates appear in Appendix B.9 along with their respective weights, and give an estimated coefficient of variation, $\hat{\beta}$, of

$$\hat{\beta} = 1.015$$

and a standard deviation estimate, δ, of

$$\delta = \beta\delta$$

$$= (1.015)\delta.$$

Since the between-laboratory component contains the within-laboratory component, it is theoretically impossible to obtain a larger within- than between-laboratory component. When the within is larger than the between, as it is here, the usual conclusion that is drawn is that there is no laboratory effect. That is, the laboratory bias component, σ_L^2, is assumed to be equal to zero.

In this case, however, that is not a reasonable conclusion. By inspection of the data, it is easy to see that there are tendencies among the collaborators to be consistently higher or lower than the rest, most notably with Lab 102. The conclusion drawn in this case is that the high values are of such magnitude that they prevent the separation of within-laboratory and laboratory bias terms from the total variability.

Since the between-laboratory component is free from run-to-run source variation, it is considered a good estimate of the precision of the acid mist determination with the occurrence of occasional high values. No attempt is made to partition this component into its within-laboratory and laboratory bias components.

V. PRECISION OF METHOD 8 WITH HIGH VALUES EXCLUDED

As discussed previously, there is no information available to show whether the high H_2SO_4/SO_3 values (in excess of 60 lb/scf $\times 10^{-7}$) are typical of Method 8 results or whether there were factors peculiar to the test site or test period which caused their occurrence. If these values are atypical, then they should not be used in the data analysis, since they would unfairly bias the results. To account for this possibility, a second analysis is performed on each data set with these runs excluded. Due to the significant negative correlation between the SO_2 and H_2SO_4/SO_3 determinations, the SO_2 determinations corresponding to the high acid mist values are also eliminated from the data set for the second analysis. This results in 46 determinations used in the analyses blocked in the same manner as the complete data set.

A. SO_2

The distributional characteristics of the determinations remain unchanged. The linear transformation provides the highest degree of equality of variance. This implies that the within- and between-laboratory variances, σ^2 and σ_b^2, are independent of the mean level. The estimates are obtained using the pooled variance technique as before.

The run data provide 14 estimates of σ_b^2, and these are shown in Table B.15. Substituting into the formula gives

$$\delta_b^2 = 5111.79$$

and

$$\delta_b = \sqrt{5111.79}$$

$$= 71.50 \text{ lb/scf} \times 10^{-7}$$

with 3 degrees of freedom. For the 46 determinations, the sample mean is $\bar{\delta} = 448.67$ lb/scf $\times 10^{-7}$. Using this, the coefficient of variation for the between-laboratory component is

$$\hat{\beta}_b = \frac{\delta_b}{\bar{\delta}}$$

$$= \frac{71.50}{448.67}$$

$$= 0.16.$$

There are 12 estimates of σ^2 obtained from the collaborator-block data, and these are summarized in Table B.16. Pooling these estimates gives

$$\delta^2 = 4351.42$$

with 34 degrees of freedom. From this, the estimated standard deviation is

$$\delta = \sqrt{4351.42}$$

$$= 65.97 \text{ lb/scf} \times 10^{-7}.$$

The estimated coefficient of variation, then, is

$$\hat{\beta} = \frac{\hat{\sigma}}{\bar{\delta}}$$

$$= \frac{65.97}{448.67}$$

$$= 0.15.$$

The laboratory bias variance, σ_L^2, is estimated as

$$\sigma_L^2 = \sigma_b^2 - \sigma^2$$

$$= 5111.79 - 4351.42$$

$$= 760.37$$

and the laboratory bias standard deviation estimate is

$$\sigma_L = \sqrt{\sigma_L^2}$$

$$= \sqrt{760.37}$$

$$= 27.57 \text{ lb/scf} \times 10^{-7}$$

This gives an estimated laboratory bias coefficient of variation of

$$\hat{\beta}_L = \frac{\sigma_L}{\bar{\delta}}$$

$$= \frac{27.37}{448.67}$$

$$= 0.06.$$

B. H_2SO_4/SO_3

The 46 acid mist determinations are shown in Appendix B.10 to have the same distributional nature as the full data set. That is, the logarithmic transformation is the best suited to the data which implies a proportional relationship between the true mean and the true standard deviation. The estimation procedures of Appendices B.7 and B.8 are used to obtain estimates of the coefficients of variation for the within- and between-laboratory components.

The between-laboratory coefficient of variation, β_b, is estimated by using a weighted combination of the run beta estimates. This gives

$$\hat{\beta}_b = 0.661$$

and an estimated between-laboratory standard deviation of

$$\sigma_b = \hat{\beta}_b \delta$$

$$= (0.661)\delta.$$

There are 3 degrees of freedom associated with this estimate.

The collaborator-block data provide 12 estimates of the within-laboratory coefficient of variation, β. Combining these gives an estimated value of

$$\hat{\beta} = (0.585).$$

The within-laboratory standard deviation, then, is

$$\hat{\sigma} = \hat{\beta}\delta$$

$$= (0.585)\delta$$

with 42 degrees of freedom.

The laboratory bias standard deviation, σ_L, is estimated by

$$\sigma_L = \sqrt{\hat{\sigma}_b^2 - \hat{\sigma}^2}$$

$$= \sqrt{\hat{\beta}_b^2\delta^2 - \hat{\beta}^2\delta^2}$$

$$= \sqrt{(\hat{\beta}_b^2 - \hat{\beta}^2)\,\delta^2}$$

$$= \sqrt{[(0.661)^2 - (0.585)^2]\,\delta^2}$$

$$= \sqrt{(0.095)\delta^2}$$

$$= (0.308)\delta.$$

VI. PRECISION AND ACCURACY OF ANALYTICAL PHASE

A. The Unknown Sulfate Solution Test

An unknown sulfate solution test was conducted as part of the Method 8 collaborative study to assess the precision and accuracy of the analytical phase of Method 8 separately. Three different sulfate solutions, with the actual concentrations concealed, were provided to each of the four collaborative laboratory teams for sample analysis by the Method 8 barium-thorin titration procedure along with the collaborative test samples. Sample aliquots of 10 mℓ each from each solution were analyzed by each collaborative team in triplicate on each of three of the sample analysis days. The instruction and reporting form for the unknown sulfate solution test is illustrated in Figure 5. The reported data are presented and summarized in Tables B.20 and B.21 of Appendix B.11.

It should be noted that the sulfuric acid mist/sulfur trioxide and the sulfur dioxide sample fractions are analyzed separately by the same barium-thorin titration procedure in Method 8. Hence, the precision estimates and accuracy statements derived in this section from the unknown sulfate solution test data pertain to the Method 8 analytical phase concentration determinations of both sulfuric acid mist and sulfur dioxide.

B. Analytical Phase Precision

A separate analysis of variance has been performed on the data for each of the three unknown sulfate solution concentrations. These analyses of variance, described in Appendix B.11, utilized a random effects model to analyze the importance of the laboratory bias (collaborator) and within-laboratory (day and replication) components of the analytical phase variance. Because Lab 104 consistently obtained determinations that were from 6 to 9 percent too low, a significant large laboratory bias component occurred with every solution. The day factor was only significant for the solution with the highest SO_2 concentration.

Table 5. Method 8 Analytical Phase Precision Estimates

Precision Measure	Component Estimates	
	Coefficient of Variation	Standard Deviation
Within-Laboratory	–	$\hat{\sigma} = 2.19 \times 10^{-7}$ lb/scf
Laboratory Bias	$\hat{\beta}_L = 0.0353$	$\hat{\sigma}_L = (0.0353)\delta$
Between-Laboratory	$\hat{\beta}_b = 0.0368$	$\hat{\sigma}_b = (0.0368)\delta$

The analytical phase precision estimates developed from the analysis of variance are presented in Table 5. A constant within-laboratory standard deviation estimate $\hat{\sigma} = 2.19 \times 10^{-7}$ lb/scf was obtained from the pooled within-laboratory variance, because the within-laboratory variance remained quite stable with increasing solution concentration. Hence, there is no constant within-laboratory coefficient of variation for the analytical phase. The laboratory bias standard deviation, $\hat{\sigma}_L = 0.0353\delta$, and the between-laboratory standard deviation, $\hat{\sigma}_b = 0.0368\delta$, were derived by the coefficient of variation technique of Appendices B.7 and B.8. Note that since the within-laboratory component is constant, laboratory bias is the major component of the between-laboratory variability of the Method 8 analytical phase in the normal range of concentrations.

C. Analytical Phase Accuracy

In this report, the accuracy of a procedure refers to its ability to obtain, on the average, the true value of the quantity being measured, taking into account the precision uncertainty that has been determined for the procedure. To phrase the definition in statistical terminology, an accurate procedure is one that is unbiased within the procedure's precision. Hence, a statement regarding a procedure's accuracy connotes nothing about the procedure's precision (i.e., its ability to repeatedly obtain the same value in measuring a fixed quantity).

The accuracy of the analytical phase of Method 8 is examined by comparing the average of all the collaborators' determinations of the SO_2 concentration for a given unknown solution against the "true" effective SO_2 concentration represented by that sulfuric acid solution. This comparison is shown in Table 6.

Table 6. Accuracy of the Analytical Phase of Method 8

Sulfur Dioxide Concentration, 10^{-7} lb/scf						
Solution	Prepared "True" Value	Mean Over All Collaborators	Difference	95-Percent Confidence Level		Percentage Difference
				Range	Interval About Mean	
C	158.6	156.9	− 1.7	± 6.0	(150.9, 162.9)	−1.1
A	423.0	410.1	−12.9	±14.4	(395.7, 424.5)	−3.0
B	669.8	653.5	−16.3	±22.7	(630.8, 676.2)	−2.4

The 95-percent confidence range and interval for the mean over all collaborators is based on a standard deviation of $\sqrt{\delta_L^2/4 + \delta^2/3} = \sqrt{(0.0853\delta)^2/4 + (2.19 \times 10^{-7}\ \text{lb/scf})^2/3}$.

All the Method 8 solution means were lower (from 1.1 to 3.0 percent) than their respective "true" values. But inspection of Table 6 shows that for all three solutions the prepared "true" SO_2 concentration level lies within the 95-percent confidence interval about the collaborators' mean Method 8 determination. Therefore, the analytical phase of Method 8 is unbiased within the precision of the method.

D. Comparison With Method 6

The same barium-thorin titration procedure is utilized for sample analysis both in Method 8 and in Method 6. Furthermore, the unknown sulfate solution tests performed with the Method 8 and the Method 6 collaborative tests both specified use of a 10 mℓ sample aliquot and addition of 40 mℓ of isopropanol. Since they are both derived from the unknown sulfate solution test data, the analytical phase precision and accuracy findings for Method 8 should be comparable to the Method 6 analytical phase precision and accuracy presented in our Method 6 collaborative test report.[4]

The analytical phase precision point estimates obtained for each unknown solution in both the Method 6 and the Method 8 collaborative studies are tabulated as Table 7. The actual analytical phase precision estimates

Table 7. Comparison of Method 6 and Method 8 Analytical Phase Precision Data

Method	Unknown Solution	Mean, 10^{-7} lb/scf			Within Laboratory	Laboratory Bias		Between-Laboratory	
		True	Method 6	Method 8	Std. Dev.	Std. Dev.	Coef. of Var.	Std. Dev.	Coef. of Var.
6	B	0.0	0.1		0.41	0.49	–	0.64	–
8	C	158.6		156.9	2.82	5.47	0.0345	6.16	0.0388
6	D	176.3	174.4		2.68	4.41	0.0250	5.16	0.0293
6	A	352.5	349.0		4.16	6.68	0.0189	7.87	0.0223
8	A	423.0		410.1	1.24	16.09	0.0380	16.14	0.0382
6	C	528.8	522.0		3.23	11.09	0.0210	11.55	0.0218
8	B	669.8		653.5	2.20	22.33	0.0333	22.44	0.0335

obtained using all the unknown solution estimates except those for the blank solution B of Method 6 are summarized in Table 8 both for Method 6 and Method 8. There is reasonably good agreement between the Method 6 and Method 8 precision estimates. Method 6 had the higher within-laboratory precision variation, while Method 8 exhibited more laboratory bias and between-laboratory variation. Given the relatively small magnitude of these discrepancies, they are probably attributable to the normal random variation to be expected between different sets of four laboratories and four analysts performing the same procedures. Combined estimates of the analytical phase precision standard deviations of the barium-thorin titration procedure are also presented in Table 8. The within-laboratory estimate was derived by pooling the Method 6 and Method 8 variances estimates, with each method's estimate given equal weight. The laboratory bias and between-laboratory estimates were obtained by averaging the two methods' coefficients of variation for each precision component.

A summary of the Method 6 and Method 8 evidence regarding the accuracy of their analytical phase barium-thorin titration procedure is presented in Table 9. Both in Method 6 and Method 8, the barium-thorin

Table 8. Analytical Phase Standard Deviation Estimate Comparison

Precision Component	Method 6 Estimates	Method 8 Estimates	Combined Barium-Thorin Titration Estimates
Within-Laboratory	$\hat{\sigma} = 3.41 \times 10^{-7}$ lb/scf	$\hat{\sigma} = 2.19 \times 10^{-7}$ lb/scf	$\hat{\sigma} = 2.86 \times 10^{-7}$ lb/scf
Laboratory Bias	$\hat{\sigma}_L = (0.0219)\,\delta$	$\hat{\sigma}_L = (0.0353)\,\delta$	$\hat{\sigma}_L = (0.0286)\,\delta$
Between-Laboratory	$\hat{\sigma}_b = (0.0245)\,\delta$	$\hat{\sigma}_b = (0.0368)\,\delta$	$\hat{\sigma}_b = (0.0306)\,\delta$

Table 9. Accuracy of the Barium-Thorin Titration Procedure

Method	Unknown Solution	Sulfur Dioxide Concentration, 10^{-7} lb/scf					Percentage Difference
		Prepared "True Value"	Method 6 Mean	Method 8 Mean	Difference	95-Percent Confidence Interval About Mean	
6	B	0.0	0.1		+0.1	(−0.4, 0 6)	–
8	C	158.6		156.9	−1.7	(150.9, 162.9)	−1.1
6	D	176.3	174.4		−1.9	(170.6, 178.2)	−1.1
6	A	352.5	349.0		−3.5	(341.4, 356.6)	−1.0
8	A	423.0		410.1	−12.9	(395.7, 424.5)	−3.0
6	C	528.8	522.0		−6.8	(510.6, 533.4)	−1.3
8	B	669.8		653.5	−16.3	(630.8, 676.2)	−2.4

titration procedure consistently yields SO_2 concentration determinations that are slightly (i.e., from 1.0 percent to 3.0 percent) below the true value. However, for each unknown solution, the prepared "true" value lies within the 95 percent confidence interval about the mean value. Therefore, the barium-thorin titration procedure utilized in the analytical phases of Method 6 and Method 8 is accurate within its limits of precision. The consistently slightly low average readings obtained with the procedure apparently result from a low-value bias by some of the collaborative laboratories.

APPENDIX A

METHOD 8—DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

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METHOD 8—DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. A gas sample is extracted from a sampling point in the stack and the acid mist including sulfur trioxide is separated from sulfur dioxide. Both fractions are measured separately by the barium-thorin titration method.

1.2 Applicability. This method is applicable to determination of sulfuric acid mist (including sulfur trioxide) and sulfur dioxide from stationary sources only when specified by the test procedures for determining compliance with the New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling. See Figure 8-1. Many of the design specifications of this sampling train are described in APTD-0581.

2.1.1 Nozzle—Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe—Pyrex[1] glass with a heating system to prevent visible condensation during sampling.

2.1.3 Pitot tube—Type S, or equivalent, attached to probe to monitor stack gas velocity.

2.1.4 Filter holder—Pyrex[1] glass.

2.1.5 Impingers—Four as shown in Figure 8-1. The first and third are of the Greenburg-Smith design with standard tip. The second and fourth are of the Greenburg-Smith design, modified by replacing the standard tip with a ½-inch ID glass tube extending to one-half inch from the bottom of the impinger flask. Similar collection systems, which have been approved by the Administrator, may be used.

2.1.6 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5° F., dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer—To measure atmospheric pressure to ±0.1 inch Hg.

[1] Trade name.

2.2 Sample recovery.

2.2.1 Wash bottles—Two.

2.2.2 Graduated cylinders—250 ml., 500 ml.

2.2.3 Glass sample storage containers.

2.2.4 Graduated cylinder—250 ml.

2.3 Analysis.

2.3.1 Pipette—25 ml., 100 ml.

2.3.2 Burette—50 ml.

2.3.3 Erlenmeyer flask—250 ml.

2.3.4 Graduated cylinder—100 ml.

2.3.5 Trip balance—300 g. capacity, to measure to ±0.05 g.

2.3.6 Dropping bottle—to add indicator solution.

3. *Reagents.*

3.1 Sampling.

3.1.1 Filters—Glass fiber, MSA type 1106 BH, or equivalent, of a suitable size to fit in the filter holder.

3.1.2 Silica gel—Indicating type, 6-16 mesh, dried at 175° C. (350° F.) for 2 hours.

3.1.3 Water—Deionized, distilled.

3.1.4 Isopropanol, 80%—Mix 800 ml. of isopropanol with 200 ml. of deionized, distilled water.

3.1.5 Hydrogen peroxide, 3%—Dilute 100 ml. of 30% hydrogen peroxide to 1 liter with deionized, distilled water.

3.1.6 Crushed ice.

3.2 Sample recovery.

3.2.1 Water—Deionized, distilled.

3.2.2 Isopropanol, 80%.

3.3 Analysis.

3.3.1 Water—Deionized, distilled.

3.3.2 Isopropanol.

3.3.3 Thorin indicator—1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt (or equivalent). Dissolve 0.20 g. in 100 ml. distilled water.

3.3.4 Barium perchlorate (0.01*N*)—Dissolve 1.95 g. of barium perchlorate [$Ba(ClO_4)_2 \cdot 3H_2O$] in 200 ml. distilled water and dilute to 1 liter with isopropanol. Standardize with sulfuric acid.

3.3.5 Sulfuric acid standard (0.01*N*)—Purchase or standardize to ± 0.0002 *N* against 0.01 *N* NaOH which has previously been standardized against primary standard potassium acid phthalate.

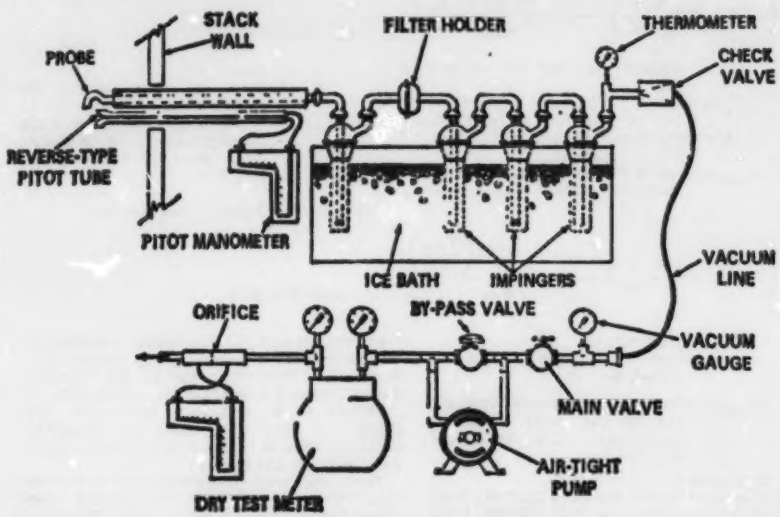

Figure 8-1. Sulfuric acid mist sampling train.

4. *Procedure.*

4.1 Sampling.

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of collection train. Place 100 ml. of 80% isopropanol in the first impinger, 100 ml. of 3% hydrogen peroxide in both the second and third impingers, and about 200 g. of silica gel in the fourth impinger. Retain a portion of the reagents for use as blank solutions. Assemble the train without the probe as shown in Figure 8-1 with the filter between the first and second impingers. Leak check the sampling train at the sampling site by plugging the inlet to the first impinger and pulling a 15-inch Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at a vacuum of 15 inches Hg is acceptable. Attach the probe and turn on the probe heating system. Adjust the probe heater setting during sampling to prevent any visible condensation. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 70° F. or less.

4.1.3 Train operation. For each run, record the data required on the example sheet shown in Figure 8-2. Take readings at each sampling point at least every 5 minutes and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Start the pump and immediately adjust the flow to isokinetic conditions. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. At the conclusion of each run, turn off the pump and record the final readings. Remove the probe from the stack and disconnect it from the train. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes.

4.2 Sample recovery.

4.2.1 Transfer the isopropanol from the first impinger to a 250 ml. graduated cylinder. Rinse the probe, first impinger, and all connecting glassware before the filter with 80% isopropanol. Add the rinse solution to the cylinder. Dilute to 250 ml. with 80% isopropanol. Add the filter to the solution, mix, and transfer to a suitable storage container. Transfer the solution from the second and third impingers to a 500 ml. graduated cylinder. Rinse all glassware between the filter and silica gel impinger with deionized, distilled water and add this rinse water to the cylinder. Dilute to a volume of 500 ml. with deionized, distilled water. Transfer the solution to a suitable storage container.

4.3 Analysis.

4.3.1 Shake the container holding isopropanol and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample. Pipette a 100 ml. aliquot of sample into a 250 ml. Erlenmeyer flask and add 2 to 4 drops of thorin indicator. Titrate the sample with barium perchlorate to a pink end point. Make sure to record volumes. Repeat the titration with a second aliquot of sample. Shake the container holding the contents of the second and third impingers. Pipette a 25 ml. aliquot of sample into a 250 ml. Erlenmeyer flask. Add 100 ml. of isopropanol and 2 to 4 drops of thorin indicator. Titrate the sample with barium perchlorate to a pink end point. Repeat the titration with a second aliquot of sample. Titrate the blanks in the same manner as the samples.

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5. *Calibration.*

5.1 Use standard methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater.

5.2 Standardize the barium perchlorate with 25 ml. of standard sulfuric acid containing 100 ml. of isopropanol.

6. *Calculations.*

6.1 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F., 29.92 inches Hg) by using Equation 8-1.

PLANT_____
LOCATION_____
OPERATOR_____
DATE_____
RUN NO._____
SAMPLE BOX NO._____
METER BOX NO._____
METER $\Delta H@$_____
C FACTOR_____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE_____
BAROMETRIC PRESSURE_____
ASSUMED MOISTURE, %_____
HEATER BOX SETTING_____
PROBE LENGTH, in._____
NOZZLE DIAMETER, in._____
PROBE HEATER SETTING_____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (P_g), in. Hg.	STACK TEMPERATURE (T_s), °F	VELOCITY HEAD (Δp),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), in. H_2O	GAS SAMPLE VOLUME (V_m), ft.³	GAS SAMPLE TEMPERATURE AT DRY GAS METER		SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
							INLET ($T_{m_{in}}$), °F	OUTLET ($T_{m_{out}}$), °F		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

Figure 8-2. Field data.

$$V_{m_{std}} = V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71\frac{°R}{\text{in. Hg}}\right)V_m\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{T_m}\right) \qquad \text{equation 8-1}$$

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

ΔH = Pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.2 Sulfuric acid concentration.

$$C_{H_2SO_4} = \left(1.08\times10^{-4}\frac{\text{lb.-l.}}{\text{g.-ml.}}\right)\frac{(V_t - V_{tb})(N)\left(\frac{V_{soln}}{V_a}\right)}{V_{m_{std}}} \qquad \text{equation 8-2}$$

where:

$C_{H_2SO_4}$ = Concentration of sulfuric acid at standard conditions, dry basis, lb./cu. ft.

1.08×10^{-4} = Conversion factor including the number of grams per gram equivalent of sulfuric acid (49 g./g.-eq.), 453.6 g./lb., and 1,000 ml./l., lb.-l./g.-ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

N = Normality of barium perchlorate titrant, g.-eq./l.

V_{soln} = Total solution volume of sulfuric acid (first impinger and filter), ml.

V_a = Volume of sample aliquot titrated, ml.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft., see Equation 8-1.

6.3 Sulfur dioxide concentration.

$$C_{SO_2} = \left(7.05\times10^{-5}\frac{\text{lb.-l.}}{\text{g.-ml.}}\right)\frac{(V_t - V_{tb})(N)\left(\frac{V_{soln}}{V_a}\right)}{V_{m_{std}}} \qquad \text{equation 8-3}$$

where:

C_{SO_2} = Concentration of sulfur dioxide at standard conditions, dry basis, lb./cu. ft.

7.05×10^{-5} = Conversion factor including the number of grams per gram equivalent of sulfur dioxide (32 g./g.-eq.) 453.6 g./lb., and 1,000 ml./l., lb.-l./g.-ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

N = Normality of barium perchlorate titrant, g.-eq./l.

V_{soln} = Total solution volume of sulfur dioxide (second and third impingers), ml.

V_a = Volume of sample aliquot titrated, ml.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft., see Equation 8-1.

7. *References.*

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APPENDIX B

STATISTICAL METHODS

APPENDIX B. STATISTICAL METHODS

This appendix is composed of various independent sections each of which contains a statistical analysis pertinent to a particular question or problem encountered in the analysis of the Method 8 collaborative test data. References to these sections have been made at various junctures in the body of the report.

B.1 Preliminary Data Analysis

The original Method 8 test data appears in Table B.1. This table lists the sulfur dioxide concentration determinations, C_{SO_2}, and the acid mist concentration determinations, $C_{H_2SO_4}$, for the 14 runs as reported by the four collaborating laboratories. These quantities were recomputed from the raw data for several runs from each laboratory to detect systematic and random calculation errors. All discovered calculation errors that exceed acceptable round-off error were corrected. When a systematic calculation error was found, the calculations were rechecked for all the laboratory's runs.

An outlier analysis was performed on the corrected data. Any determination which differed by more than 40 percent from the closest corresponding value obtained by any of the other three collaborators for that run was subjected to further scrutiny. Such potential outliers were to be rejected only if physical evidence showed them to be invalid determinations.

Table B.1. Originally Reported Collaborative Test Data
(lb/scf × 10^{-7})

Run	Lab 101		Lab 102		Lab 103		Lab 104	
	C_{SO_2}	$C_{H_2SO_4}$	C_{SO_2}	$C_{H_2SO_4}$	C_{SO_2}	$C_{H_2SO_4}$	C_{SO_2}	$C_{H_2SO_4}$
1	469	38.3	*	*	226	64.3	506	6.0
2	319	111.6	*	*	455	31.9	578	10.5
3	393	49.0	204†	27.9†	367	11.7	233	7.1
4	319	45.4	161	5.0	298	24.2	284	4.2
5	382	8.7	108	5.3	341	10.1	400	12.4
6	412	7.9	198	5.5	377	14.1	†	†
7	423	3.3	226	6.7	166	112.9	491	7.0
8	436	9.9	225	8.6	402	11.1	438	22.2
9	484	11.6	240	8.3	444	13.9	564	7.5
10	466	13.5	174	8.6	327	8.6	242	112.9
11	306	98.8	235	6.3	432	8.6	514	18.9
12	468	76.1	239	5.7	441	9.3	552	25.8
13	492	7.8	232	10.2	459	12.7	379	22.8
14	480	6.3	227	6.6	438	7.0	582	22.9

*Run not made.
†Run not completed due to equipment problems.

Through this process, several systematic calculation problems were discovered. Throughout the collaborative test Lab 101 experienced erratic and unreliable operation of its digital temperature indicator for measuring the dry gas meter temperature. For this reason, Lab 101 usually estimated T_m, the average dry gas meter temperature, as 10 deg above the ambient temperature, T_a($T_m = T_a + 10°$). However, the Lab 101 meter temperature estimation was inconsistent, taking on values of $T_m = T_a + 20°$ on run 1, $T_m = T_a - 10°$ on run 3 and $T_m = T_a + 14°$ on run 7. Lab 103, which used identical equipment, also experienced difficulty with its digital temperature indicator, but used an auxiliary thermocouple harness and portable thermocouple to obtain T_m. These values usually differed by less than 3 degrees from T_a. Hence, to obtain consistency, $T_m = T_a$ was used to re-estimate the Lab 101 dry gas meter temperatures for each run. This slight change in T_m produced correspondingly small changes in the determined concentrations.

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The outlier analysis revealed that the sulfur dioxide concentrations reported by Lab 102 were consistently low by about a factor of 2, but no error could be found in the calculations. Through discussion with Lab 102 personnel, it was learned that a factor of 2.5 was required to obtain the actual concentrations. A special note to the collaborators specified the use of a 10-mℓ aliquot in determining the SO_2 concentration rather than the 25-mℓ aliquot as in the *Federal Register*.[3] The analysts used the 10-mℓ aliquot, but upon performing the calculations, inserted 25 mℓ into the equation. Hence, each reported concentration had to be multiplied by 2.5 to obtain the actual concentration of SO_2 determined by Lab 102.

There are four missing values in each data set. Lab 102 was not present at the beginning of the test period and missed the first run. During the second run, Lab 102's equipment was not fully assembled and they were unable to participate in that run. On run 3, Lab 102 was forced to abort the run due to a broken carriage after completing only one traverse, and thus their determination was not usable. On run 6, broken glassware caused Lab 104 to abort the sampling run. The statistical analyses were based upon the remaining 52 determinations, with no substitutions made for these missing values.

B.2 Negative Correlation in the Concurrent Concentration Determinations of Sulfur Dioxide and Sulfuric Acid Mist

When a test method specifies making multiple chemical determinations using connected apparatus from a single sampling run, an important consideration is whether the determinations are independent of each other. For Method 8, the question is whether the sulfur dioxide concentration determination for a run is correlated with the sulfuric acid mist concentration determination.

Intuitively, one would expect some positive correlation to exist between the true sulfuric acid mist concentration and the true sulfur dioxide concentration in the stack. This intuitive expectation follows from the consideration that plant process changes that would cause an increase (decrease) in stack sulfuric acid mist concentration would be likely to produce an increase (decrease) in stack sulfur dioxide concentration.

In Figure B.1, the sulfur dioxide concentration determination for a run is plotted against the sulfuric acid mist concentration determination for that same run for the 52 pairs of values. Figure B.1 indicates that, contrary to expectation, a significant negative correlation may exist, i.e., a high acid mist value is accompanied by a low SO_2 value. The correlation coefficient for the 52 pairs is calculated, as are the correlation coefficients for each laboratory's results separately, and these are shown in Table B.2.

Using the test statistic[2]

$$t_c = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}},$$

the significance level (α) of each correlation coefficient can be determined. The null hypothesis is that the true correlation coefficient, ρ, is equal to zero. The test statistic follows Student's t distribution with $n-2$ degrees of freedom. Using a significance level of 5 percent, the combined correlation coefficient and those from Labs 101 and 103 are shown to be significant, while the Lab 102 and 104 data are not.

If all acid mist determinations above 60 lb/scf $\times 10^{-7}$ are eliminated, a correlation coefficient can be computed for the remaining 46 pairs. The value of $r = -0.1355$ is not significantly different from zero, and 60 lb/scf $\times 10^{-7}$ is chosen as the cutoff point for a high value.

There are 6 high values for the complete data set, with 3 from Lab 101, 2 from Lab 103, 1 from Lab 104 and none from Lab 102. This also suggests that the negative correlation is related to the high value phenomenon, since the more high values present, the higher the degree of negative correlation for that lab.

Table B.2. Correlation of Concurrent Method 8 Determinations of H_2SO_4 and SO_2

Laboratory	Runs, n	Number of H_2SO_4 Determ. Above 60×10^{-7} lb/scf	Correlation Coefficient, r	Test Statistic, $r\sqrt{n-2}/\sqrt{1-r^2}$	Significance of Correlation, $\hat{a}$
All	52	6	−0.5105	−4.198	<0.0001
101	14	3	−0.6276	−2.793	0.009
102	11	0	+0.4186	1.383	0.10
103	14	2	−0.7947	−4.535	0.0005
104	13	1	−0.3862	−1.388	0.10
All–With H_2SO_4 Determinations Above 60×10^{-7} lb/scf Excluded	46	0	−0.1355	−0.907	0.19

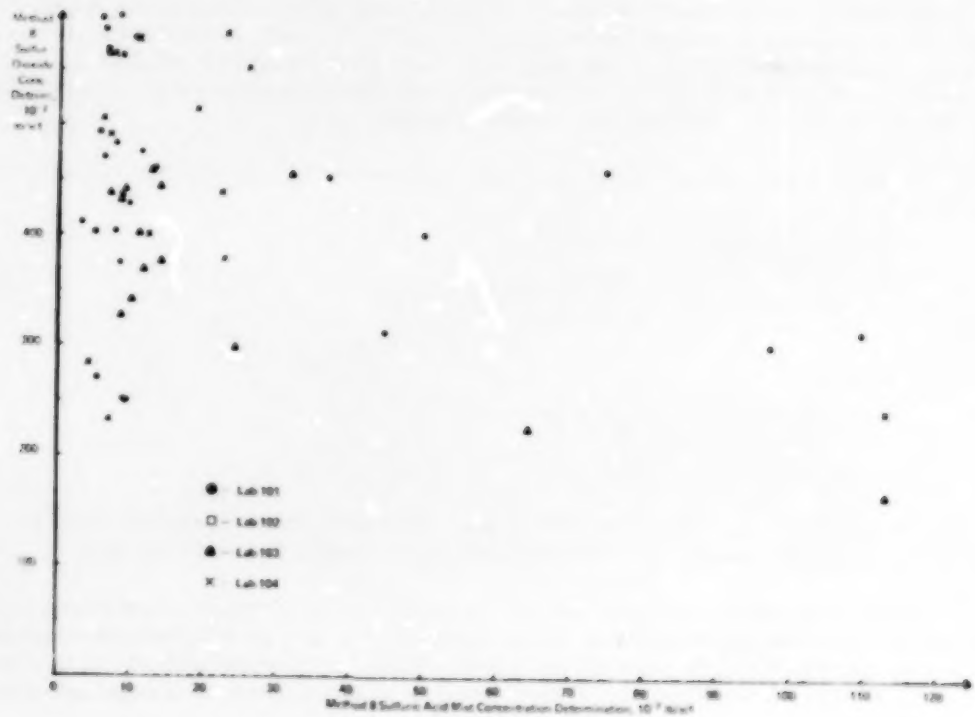

Figure B.1. Negative Correlation of Concurrent Method 8 Determinations

B.3. Blocking the Determinations

In order to obtain good estimates of the within-laboratory precision associated with Method 8 determinations it is necessary to group the runs into blocks where the true mean concentration on each run is essentially the same. Friedman's rank test[7] is used to test the hypothesis that all the run means are equal.

The Friedman test is a two-way analysis of variance based upon the ranks of the observations. The factors for this test are runs and laboratories, with laboratories serving as a blocking factor. The determinations for each laboratory are ranked from lowest to highest, then a rank sum, R_j, for each run is computed. The test statistic is

$$\chi_r^2 = \frac{12}{n(k)(k+1)} \sum_{j=1}^{k} R_j^2 - 3n(k+1)$$

where

n – the number of labs

k – the number of runs.

The test statistic follows an approximate chi-square distribution with $k - 1$ degrees of freedom.

For this test, the high values (>60 lb/scf × 10^{-7}) for acid mist and their associated SO_2 values are not used. While it cannot be determined that these are invalid results, they clearly do not represent the true stack concentration, which is under consideration here. These values are assigned the median rank of 7.5, as are the missing values in the data set. This will affect the determined significance level, but in this case it is felt that the result will be to make the test more conservative.

The ranks for the corrected SO_2 data from Table 1 are shown in Table B.3. The test statistic for the SO_2 data is

$$\chi_r^2 = \frac{12}{4(14)(15)} \sum_{j=1}^{14} R_j^2 - 3(4)(15)$$

$$= \frac{12}{840} [(34)^2 + \ldots + (46)^2] - 180$$

$$= 36.91$$

Comparing this to a chi-square distribution with 13 degrees of freedom, the significance level is less than 0.001. Thus, there is significant variation in the run mean levels, and blocking of the runs must be done.

The blocks are established using the concurrent data that was taken during the test, and is discussed in Section III. To demonstrate that this is an effective scheme, the Friedman test is applied to the blocks separately. The summaries of these tests are shown in Table B.4. The significance levels associated with the three blocks are 0.273, 0.116 and 0.068, respectively. None of these show significant differences in mean levels at the 5 percent level.

Similarly, the acid mist determinations are tested for equality of run means. With the high values eliminated, the rank sums are computed, as shown in Table B.5. The test statistic is $\chi_r^2 = 6.78$ with 13 degrees of freedom. The significance level associated with this value is 0.913, and the hypothesis cannot be rejected. Thus, there is no blocking required, and the determinations may be treated as 14 repetitions at the same true mean concentration.

B.4 Distributional Nature of SO_2 Determinations

In order to obtain information about the distributional nature of the determinations, the corrected values are tested for equality of variance using Bartlett's test.[2] In addition, the determinations are transformed using

Table B.3. Friedman Rank Test, All SO_2 Runs

Run	Labs				R_j
	101	102	103	104	
1	10	7.5*	7.5†	9	34
2	7.5†	7.5*	13	13	41
3	3	7.5*	4	1	15.5
4	1	2	1	2	6
5	2	1	3	4	10
6	4	4	5	7.5*	20.5
7	5	7.5	7.5†	6	26
8	7.5	5	6	5	23.5
9	13	14	12	12	51
10	11	3	2	7.5†	23.5
11	7.5†	12	9	10	38.5
12	7.5†	13	11	11	42.5
13	14	11	14	3	42
14	12	10	10	14	46

H_0: All run means are equal.
Test Statistic: $\chi_r^2 = 36.91$.
Significance Level: $\hat{\alpha} < 0.001$.
Conclusion: Reject H_0.

*Missing value.
†High value (above 60 lb/scf $\times 10^{-7}$).

Table B.4. Friedman Rank Test, SO_2 Blocks

Block	Run	Labs				R_j
		101	102	103	104	
1	4	1	2	1	1	5
	5	2	1	3	3	9
	10	3	3	2	2*	10
$\chi_r^2 = 3.50$		$df = 2$		$\hat{\alpha} = 0.273$		
2	1	5	3†	3*	4	15
	2	3*	3†	5	5	16
	3	1	3†	1	1	6
	6	2	1	3	3†	9
	7	4	5	3*	2	4
$\chi_r^2 = 7.40$		$df = 4$		$\hat{\alpha} = 0.116$		
3	8	1	1	1	2	5
	9	5	6	5	5	21
	11	3.5*	4	2	3	12.5
	12	3.5*	5	4	4	16.5
	13	6	3	6	1	16
	14	2	2	3	6	13
$\chi_r^2 = 10.25$		$df = 5$		$\hat{\alpha} = 0.068$		

*High value, assigned median rank.
†Missing value assigned median rank.

Table B.5. Friedman Rank Test, Acid Mist

Run	Labs				R_j
	101	102	103	104	
1	12	7.5*	7.5†	2	29
2	7.5†	7.5*	14	6	35
3	14	7.5*	9	4	34.5
4	13	1	13	1	28
5	5	2	5	9	21
6	4	3	12	7.5*	26.5
7	1	10	7.5†	3	21.5
8	7.5	12.5	6	11	37
9	10	11	11	5	37
10	11	12.5	5	7.5†	33.5
11	7.5†	5	2.5	10	25
12	7.5†	4	4	14	29.5
13	3	14	10	12	39
14	2	7.5	1	13	23.5

H_0: All run means equal.
Test Statistic: $\chi_r^2 = 6.78$.
Significance Level: $\hat{\alpha} = 0.913$.
Conclusion: Accept H_0.

*Missing value.
†High value not used.

two common variance-stabilizing transformations, the logarithmic and the square root, and retested. The test statistic is compared to a chi-square distribution with the appropriate degrees of freedom to determine significance levels. The results are summarized in Table B.6 for both the run and the collaborator-block data.

For both the run and the collaborator-block data the best equality is achieved by the linear or original form of the data. For the run data, the significance level indicates almost perfect agreement among the variances, even though the means varied considerably. For the collaborator-block data, the significance level would not usually indicate acceptance, but the linear is the best of the three forms. The means and standard deviations for the run data are shown in Table B.7, and for the collaborator-block data in Table B.8.

For a set of data divided into groups with possibly different means but common variance, σ^2, the method used to estimate the common variance is referred to as pooling. Define

y_{ij} – the j^{th} observation in group i

$\bar{y}_i$ – the mean of group i

s_i^2 – the i^{th} variance estimate

n_i – the size of the i^{th} group

Table B.6. SO_3 Data Transformation Summary

Data	Transformation	Test Statistic	*df*	Significance Level
Run	Linear	8.988	13	0.774
	Logarithmic	15.505	13	0.277
	Square Root	11.466	13	0.572
Collaborator-Block	Linear	28.140	11	0.003
	Logarithmic	37.670	11	<0.001
	Square Root	32.188	11	0.001

Table B.7. Sulfur Dioxide Run Summary

Block	Run	Mean Concentration, lb/scf × 10^{-7}	Standard Deviation, lb/scf × 10^{-7}	Sample Size
1	4	324.50	53.66	4
	5	346.75	55.99	4
	10	366.50	101.36	4
2	1	395.00	148.74	3
	2	449.00	132.10	3
	3	333.67	88.82	3
	6	425.00	61.26	3
	7	408.25	173.02	4
3	8	457.50	71.30	4
	9	520.75	72.77	4
	11	458.50	122.61	4
	12	512.50	74.32	4
	13	475.00	82.37	4
	14	514.75	71.09	4

Table B.8. Sulfur Dioxide Collaborator-Block Summary

Block	Collaborator	Mean Concentration, lb/scf × 10^{-7}	Standard Deviation lb/scf × 10^{-7}	Sample Size
1	Lab 101	383.00	74.32	3
	Lab 102	370.00	87.31	3
	Lab 103	322.00	21.93	3
	Lab 104	308.67	81.84	3
2	Lab 101	396.80	50.78	5
	Lab 102	529.00	49.50	2
	Lab 103	318.20	118.55	5
	Lab 104	452.00	150.86	4
3	Lab 101	436.50	69.13	6
	Lab 102	582.00	15.13	6
	Lab 103	436.00	18.94	6
	Lab 104	504.83	80.08	6

and assume

$$\sigma_1^2 = \sigma_2^2 = \ldots = \sigma_k^2 = \sigma^2$$

where

σ_i^2 – the true variance of the i^{th} group

k – the number of groups.

There are k separate estimates of σ^2, and the problem is to combine these into a single estimate. By definition, a single estimate of σ^2 is $(y_{ij} - \bar{y}_i)^2$, for any i and j. From group i, then, there are n_i of these estimates and

$$\sum_{j=1}^{n_i} (y_{ij} - \bar{y}_i)^2$$

would be the total sum of squares from group i for estimating σ^2, with $(n_i - 1)$ degrees of freedom. Combining the sums of squares for all groups gives

$$SS_{\text{Pooled}} = \sum_{i=1}^{k} \sum_{j=1}^{n_i} (y_{ij} - \bar{y}_i)^2$$

the "pooled" sums of squares. Since there are $(n_i - 1)$ degrees of freedom for each group, the "pooled" degrees of freedom are

$$df_{\text{Pooled}} = \sum_{i=1}^{k} (n_i - 1)$$

$$= \sum_{i=1}^{k} n_i - k.$$

The pooled variance estimate, s_p^2, is obtained by dividing the sums of squares by the degrees of freedom, or

$$s_p^2 = \frac{\sum_{i=1}^{k} \sum_{j=1}^{n_i} (y_{ij} - \bar{y}_i)^2}{\sum_{i=1}^{k} n_i - k}$$

But since

$$s_i^2 = \frac{\sum_{j=1}^{n_i} (y_{ij} - \bar{y}_i)^2}{n_i - 1}$$

then

$$(n_i - 1)s_i^2 = \sum_{j=1}^{n_i}(y_{ij} - \bar{y}_i)^2$$

and

$$s_p^2 = \frac{\sum_{i=1}^{k}(n_i - 1)s_i^2}{\sum_{i=1}^{k} r_i - k}.$$

Given the sample variances or standard deviations and the size of the sample, the best estimate of the common variance, σ^2, is obtained by this formula.

B.5 Precision Estimates for SO_2 Determinations

In Appendix B.4, it is shown that the SO_2 determinations can be assumed to have common variance terms for both the run data and the collaborator-block data, regardless of the mean level. To estimate these, then, the individual run and collaborator-block standard deviations are combined to give a single estimate. The method of pooling variances is also discussed in Appendix B.4. The estimate is of the form

$$s_p^2 = \frac{\sum_{i=1}^{k}(n_i - 1)s_i^2}{\sum_{i=1}^{k} n_i - k}$$

where

s_i — the standard deviation of the i^{th} sample

n_i — size of the i^{th} sample

k — the number of samples.

This method will be used to estimate both the within- and between-laboratory components.

There are 12 estimates of the within-laboratory standard deviation, σ, from the collaborator-blocks. These and the block sizes are shown in Table B.8. Substituting into the above formula gives

$$\delta^2 = \frac{\sum_{i=1}^{12}(n_i - 1)s_i^2}{\sum_{i=1}^{12} n_i - 12}$$

$$\hat{\delta}^2 = \frac{(3-1)(74.32)^2 + \ldots + (6-1)(80.08)^2}{52-12}$$

$$= \frac{236{,}804.75}{40}$$

$$= 5920.12$$

This estimate has $(n_i - 1)$ degrees of freedom associated with it from each collaborator-block for a total of 40. This gives an estimated standard deviation for the within-laboratory component of

$$\hat{\delta} = \sqrt{\hat{\delta}^2}$$

$$= \sqrt{5920.12}$$

$$= 76.94.$$

The overall mean of the 52 determinations is $\bar{\delta} = 429.77$. Using this, a within-laboratory coefficient of variation is estimated by

$$\hat{\beta} = \frac{\hat{\delta}}{\bar{\delta}}$$

$$= \frac{76.94}{429.77}$$

$$= 0.18.$$

The between-laboratory variance is estimated from the 14 run standard deviations in Table B.7. Substituting these and the run sizes into the pooled variance formula gives

$$\hat{\delta}_b^2 = \frac{\sum_{i=1}^{14} (n_i - 1)s_i^2}{\sum_{i=1}^{14} n_i - 14}$$

$$= \frac{369{,}427.00}{38}$$

$$= 9721.76$$

with 3 degrees of freedom from the four laboratories. This gives an estimated between-laboratory standard deviation of

$$\hat{\delta}_b = \sqrt{9721.76}$$

$$= 98.60$$

Using the overall mean of 429.77, this gives a coefficient of variation for between-laboratories of

$$\hat{\beta}_b = \frac{\hat{\sigma}_b}{\hat{\delta}}$$

$$= \frac{98.60}{429.77}$$

$$= 0.23.$$

The laboratory bias variance, σ_L^2, is defined as

$$\sigma_L^2 = \sigma_b^2 - \sigma^2.$$

Substituting the estimates for between- and within-laboratory gives

$$\hat{\sigma}_L^2 = \hat{\sigma}_b^2 - \hat{\sigma}^2$$

$$= 9721.76 - 5920.12$$

$$= 3801.64$$

and an estimated laboratory bias standard deviation of

$$\hat{\sigma}_L = \sqrt{3801.64}$$

$$= 61.66$$

The laboratory bias coefficient of variation is estimated as

$$\hat{\beta}_L = \frac{\hat{\sigma}_L}{\hat{\delta}}$$

$$= \frac{61.66}{429.77}$$

$$= 0.14.$$

B.6 Distributional Nature of H_2SO_4/SO_3 Determinations

As an indication of the distributional nature of the determinations, the corrected values from Table 3 are tested for their equality of variance in their original form and under two transformations, the logarithmic and the square root. Bartlett's test for homogeneity of variance[2] is used to determine the degree of equality obtained. The test statistic follows a chi-square distribution and the results, along with degrees of freedom and significance levels are shown in Table B.9.

For the run data, the logarithmic transformation provides the only acceptable form of the data. For the collaborator-block data none of the three transformations is acceptable, but the smallest value of the test statistic is obtained by the logarithmic transformation. If a logarithmic transformation is accepted, the indication is that there is a proportional relationship between the true mean and true standard deviation.

To test this further, the sample means and sample standard deviations are compared. These statistics are shown for the run data in Table B.10, and the tendency for the standard deviations and means to increase together is apparent. The paired means and standard deviations are plotted in Figure B.2.

Table B.9. Acid Mist Data Transformation Summary

Data	Transformation	Test Statistic	*df*	Significance Level
Run	Linear	48.378	13	0.000
	Logarithmic	16.246	13	0.236
	Square Root	28.702	13	0.007
Collaborator-Block	Linear	46.643	3	0.000
	Logarithmic	18.783	3	0.000
	Square Root	30.845	3	0.000

Table B.10. Acid Mist Run Summary ($lb/scf \times 10^{-7}$)

Run	Mean Concentration	Standard Deviation
1	35.8	29.2
2	50.6	52.1
3	22.9	23.5
4	19.5	19.1
5	9.1	4.5
6	32.4	53.7
7	35.8	51.4
8	12.9	6.3
9	10.3	2.9
10	35.8	51.4
11	32.7	43.3
12	28.9	31.8
13	13.3	6.6
14	10.7	8.2

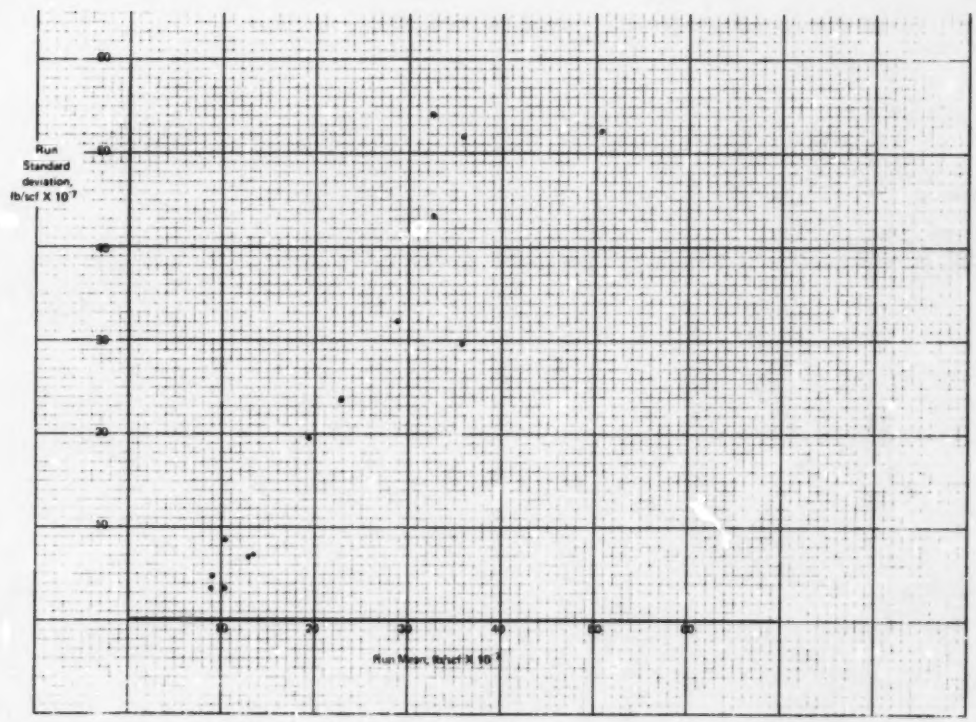

Figure B.2. Between-Laboratory Run Plot, Sulfuric Acid Mist Data

Similarly, the collaborator-block means and standard deviations are compared. These values are shown in Table B.11, and plotted in Figure B.3. Once again there is a clear tendency of the standard deviations to rise as the mean concentration rises.

From the above, models are proposed for the between- and within-laboratory standard deviations of

$$\sigma_b = \beta_b \delta$$

Table B.11. Acid Mist Collaborator-Block Summary

Block	Collaborator	Mean Concentration	Standard Deviation
1	Lab 101	34.33	36.15
	Lab 102	6.98	1.69
	Lab 103	24.31	29.62
	Lab 104	21.55	28.49

and

$$\sigma = \beta\delta$$

where β_b and β are the true coefficients of variation for between- and within-laboratory, taken to be constant. Then to estimate σ_b and σ, the coefficients of variation are estimated and $\hat{\sigma}_b$ and $\hat{\sigma}$ are defined as

$$\hat{\sigma}_b = \hat{\beta}_b\delta$$

$$\hat{\sigma} = \hat{\beta}\delta$$

where $\hat{\beta}_b$ and $\hat{\beta}$ are the estimated coefficients of variation. The standard deviations, then, are expressed as percentages of an unknown mean, δ.

B.7 Unbiased Estimation of Standard Deviation Components

In Appendix B.6, the theoretical and empirical arguments from the collaborator-block data indicate that a suitable model for the within-lab standard deviations of the acid mist data is

$$\hat{\sigma} = \hat{\beta}\delta$$

To estimate this standard deviation, we use the relationship

$$s_j = C\bar{x}_j$$

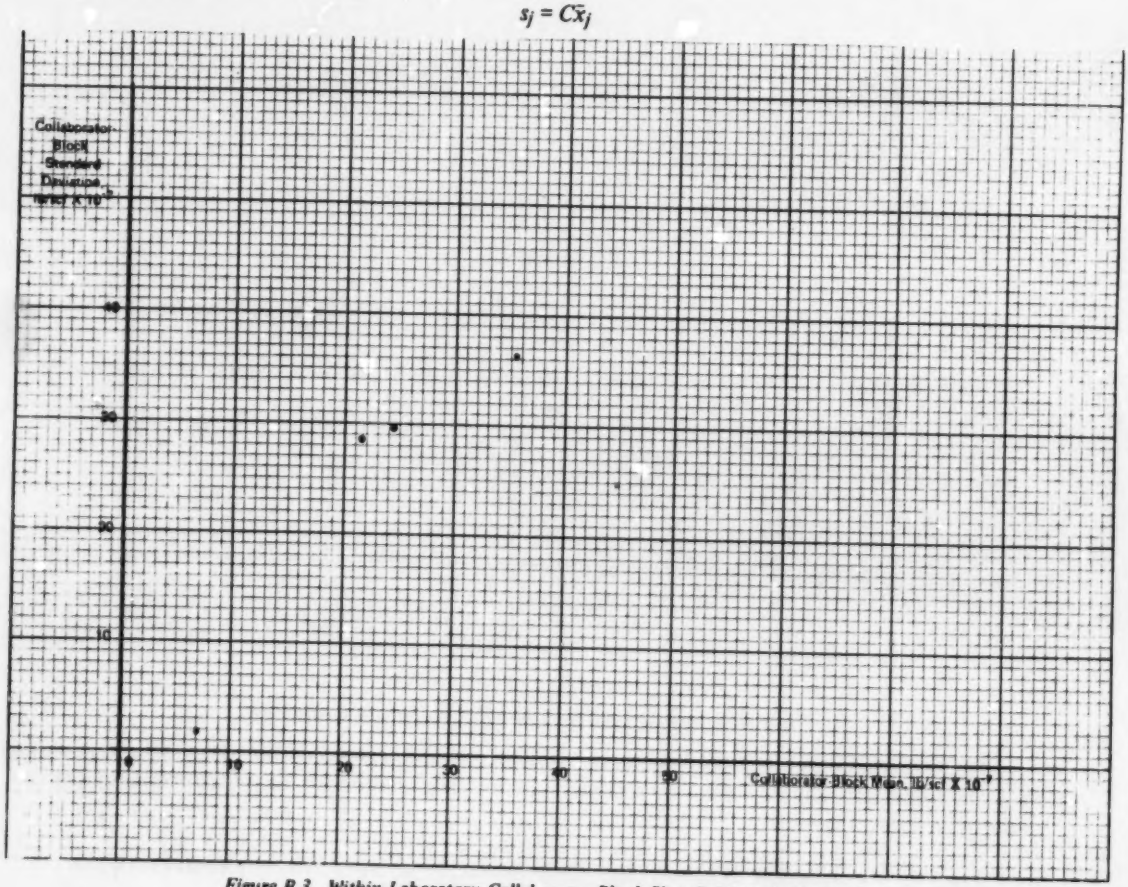

Figure B.3. Within-Laboratory Collaborator-Block Plot, Sulfuric Acid Mist

where

s_j – the collaborator-block standard deviation

$\bar{x}_j$ – the collaborator block mean

C – a constant

As previously discussed, s_j is a biased estimator for the true standard deviation, σ. The correction factor for removing the bias is dependent on the sample size n, and is given by Ziegler [8] as

$$\alpha_n = \sqrt{\frac{2}{3}} \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right)}$$

where Γ represents the standard gamma function. Thus, we can say that

$$E(\alpha_n s_j) = \sigma$$

or

$$\begin{aligned} \sigma &= \alpha_n E(s_j) \\ &= \alpha_n E(C\bar{x}_j) \\ &= \alpha_n C E(\bar{x}_j) \\ &= \alpha_n C\delta \\ &= \beta\delta \end{aligned}$$

so that in obtaining an unbiased estimate of β, we can obtain an unbiased estimate of σ as well. Thus, we *define an estimator* for σ, $\hat{\sigma}$, where

$$\hat{\sigma} = \hat{\beta}\delta.$$

From Appendices B.1 and B.2, we determined that a suitable model for the acid mist run data is

$$\sigma_b = \beta_b \delta$$

where $\sigma_b = \sqrt{\sigma_L^2 + \sigma^2}$ is the *between-lab standard deviation.* Empirically, we have

$$s_i = C_b \bar{x}_i$$

where

s_i – the run standard deviation

$\bar{x}_i$ – the run mean

C_b – a constant

and s_i is a biased estimator for σ_b. Thus, for p collaborators,

$$E(\alpha_p s_i) = \sigma$$

and we have

$$\begin{aligned} \sigma &= E(\alpha_p s_i) \\ &= \alpha_p E(C_b \bar{x}_i) \\ &= \alpha_p C_b E(\bar{x}_i) \\ &= \alpha_p C_b \delta \\ &= \beta_b \delta . \end{aligned}$$

Obtaining an estimate of β_b, we have a *new estimator*, $\hat{\sigma}_b$, of σ_b given by

$$\hat{\sigma}_b = \hat{\beta}_b \delta .$$

But $\sigma_b = \sqrt{\sigma_L^2 + \sigma^2}$ implies

$$\begin{aligned} \sigma_b^2 &= \sigma_L^2 + \sigma^2 \\ \sigma_L^2 &= \sigma_b^2 - \sigma^2 \\ \sigma_L &= \sqrt{\sigma_b^2 - \sigma^2} \end{aligned}$$

and substituting our estimates of σ_b and σ, we have

$$\begin{aligned} \hat{\sigma}_L &= \sqrt{\hat{\beta}_b^2 \delta^2 - \hat{\beta}^2 \delta^2} \\ &= \sqrt{\hat{\beta}_b^2 - \hat{\beta}^2}\ \delta , \end{aligned}$$

so that the *laboratory bias standard deviation* may be estimated as a percentage of the mean as well.

B.8 Weighted Coefficient of Variation Estimates

The technique used for obtaining estimates of the coefficients of variation of interest is to use a linear combination of the individual beta values obtained. The linear combination used will be of the form

$$\frac{1}{k} \sum_{j=1}^{k} w_j \hat{\beta}_j$$

where $\hat{\beta}_j$ is the jth coefficient of variation estimate, k is the total number of estimates, and w_j is a weight applied to the jth estimate.

As previsouly discussed, the individual estimate of β is obtained as

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

for a sample of size n. This estimator is shown in B.7 to be unbiased for the true coefficient of variation. However, since we are dealing with small samples to obtain our individual estimates, weighting is more desirable in that it provides for more contribution from those values derived from larger samples. There is more variability in the beta values obtained from the smaller samples, as can be seen by inspecting the variance of the estimator. We have that

$$\mathrm{Var}(\hat{\beta}) = \mathrm{Var}\left(\frac{\alpha_n s}{\bar{x}}\right)$$

$$= \alpha_n^2 \, \mathrm{Var}\left(\frac{s}{\bar{x}}\right)$$

$$= \alpha_n^2 \left[\frac{\beta^2}{2n}(1 + 2\beta^2)\right]$$

for normally distributed samples, [1] and true coefficient of variation, β. Rewriting this expression, we have

$$\mathrm{Var}(\hat{\beta}) = \frac{\alpha_n^2}{n}\left[\frac{\beta^2}{2}(1 + 2\beta^2)\right]$$

and all terms are constant except for α_n^2 and n. Thus, the magnitude of the variance changes with respect to the factor α_n^2/n. Now, since α_n decreases as n increases, the factor α_n^2/n must decrease as n increases, and the variance is reduced.

The weights, w_j, are determined according to the technique used in weighted least squares analysis[6], which gives a minimum variance estimate of the parameter. The individual weight, w_i, is computed as the inverse of the variance of the estimate, $\hat{\beta}_i$, and then standardized. Weights are said to be standardized when

$$\frac{1}{k}\sum_{j=1}^{k} w_j = 1$$

To standardize, the weights are divided by the average of the inverse variances for all the estimates. Thus, we can write

$$w_i = \frac{u_i}{\bar{u}}$$

where

$$u_i = \frac{1}{\mathrm{Var}(\hat{\beta}_i)}$$

and

$$\bar{u} = \frac{1}{k}\sum_{j=1}^{k} \frac{1}{\mathrm{Var}(\hat{\beta}_j)}$$

Now, from the above expressions we can determine u_i, $\bar{u}$ and w_i for the beta estimates. For any estimate, $\hat{\beta}_i$,

$$u_i = \frac{1}{\mathrm{Var}(\hat{\beta}_i)}$$

$$u_i = \frac{n_i}{\alpha_{n_i}^2}\left[\frac{2}{\beta^2(1 + 2\beta^2)}\right]$$

for sample size n_i, and

$$\bar{u} = \frac{1}{k}\sum_{j=1}^{k}\frac{1}{\mathrm{Var}(\hat{\beta}_j)}$$

$$= \frac{1}{k}\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\left[\frac{2}{\beta^2\,(1+2\beta^2)}\right]$$

$$= \frac{1}{k}\left[\frac{2}{\beta^2\,(1+2\beta^2)}\right]\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}.$$

Thus, the ith weight, w_i, is

$$w_i = \frac{u_i}{\bar{u}}$$

$$= \frac{\dfrac{n_i}{\alpha_{n_i}^2}\left[\dfrac{2}{\beta^2\,(1+2\beta^2)}\right]}{\dfrac{1}{k}\left[\dfrac{2}{\beta^2\,(1+2\beta^2)}\right]\displaystyle\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}$$

$$= \frac{\dfrac{n_i}{\alpha_{n_i}^2}}{\dfrac{1}{k}\displaystyle\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}$$

$$= \frac{\dfrac{kn_i}{\alpha_{n_i}^2}}{\displaystyle\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}.$$

The estimated coefficient of variation is

$$\hat{\beta} = \frac{1}{k}\sum_{j=1}^{k} w_j\hat{\beta}_j$$

$$= \frac{1}{k}\sum_{i=1}^{k}\frac{kn_i\alpha_{n_i}^2}{\displaystyle\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}\hat{\beta}_i$$

$$\beta = \left[\sum_{j=1}^{k} \frac{n_j}{\alpha_{n_j}^2}\right]^{-1} \sum_{i=1}^{k} \frac{n_i}{\alpha_{n_i}^2} \cdot \frac{\alpha_{n_i}\delta}{\bar{x}}$$

$$= \left[\sum_{j=1}^{k} \frac{n_j}{\alpha_{n_j}^2}\right]^{-1} \sum_{i=1}^{k} \frac{n_i\delta}{\alpha_{n_i}\bar{x}} .$$

B.9 Precision of H_2SO_4/SO_3 Determination

In Appendix B.6 the models for the standard deviations for between- and within-laboratory are determined as

$$\sigma_b = \beta_b \delta$$

and

$$\sigma = \beta\delta$$

where β_b and β are the between-laboratory and within-laboratory coefficients of variation, respectively. The coefficients of variation are taken to be constant, and the standard deviations estimated by obtaining estimates of the coefficients of variation. The manner of estimating coefficients of variation is given in Appendix B.7 and B.8.

The estimates are obtained by taking a linear combination of the individual beta estimates,

$$\hat{\beta} = \frac{1}{k} \sum_{i=1}^{k} w_i \hat{\beta}_i$$

where

$\hat{\beta}_i$ – the i^{th} estimate of the coefficient of variation

w_i – the weight assigned to the i^{th} estimate

k – the number of estimates.

There are 14 estimates of the between-laboratory coefficient of variation obtained from the run data. These are shown in Table B.12, along with their weights. The estimated between-laboratory coefficient of variation, then, is

$$\hat{\beta}_b = \frac{1}{14} \sum_{i=1}^{14} w_i \hat{\beta}_i$$

$$= \frac{1}{14}(13.411)$$

$$= 0.958$$

Table B.12. Acid Mist Run Beta Estimates and Weights

Run	Beta Hat	Weight
1	0.9203	0.760
2	1.1609	0.760
3	1.1577	0.760
4	1.0641	1.096
5	0.3567	1.096
6	0.5501	0.760
7	1.7949	1.096
8	0.5287	1.096
9	0.3110	1.096
10	1.5566	1.096
11	1.4350	1.096
12	1.1945	1.096
13	0.5384	1.096
14	0.8293	1.096

Table B.13. Acid Mist Collaborator-Block Beta Estimates and Weights

Block	Collaborator	Beta Hat	Weight
1	Lab 101	1.0735	1.080
	Lab [illegible]	0.2484	0.839
	Lab [illegible]3	1.2419	1.080
	Lab 104	1.3496	1.000

This gives an estimated standard deviation for the between-laboratory component of

$$\delta = \hat{\beta}_b \delta$$

$$= (0.958)\delta.$$

There are $4 - 1 = 3$ degrees of freedom for this estimate.

The collaborator-block data provide 4 estimates of β, the true within-laboratory coefficient of variation. This gives

$$\hat{\beta} = \frac{1}{4}\sum_{i=1}^{4} w_i \hat{\beta}_i .$$

The beta estimates and weights are shown in Table B.13. Substituting into the above formula gives

$$\hat{\beta} = \frac{1}{4}(4.060)$$

$$= 1.015.$$

There are $(n_{ij} - 1)$ degrees of freedom from each collaborator-block associated with this estimate. Summing over the four blocks gives a total of 40 degrees of freedom.

The laboratory bias coefficient of variation cannot be estimated from these data since the between-laboratory coefficient of variation is less than the within-laboratory, and hence $\hat{\beta}_b^2 - \hat{\beta}^2$ is less than zero.

B.10 Analysis of Data Excluding High Mist Values

To determine the best means of analyzing the data with the high mist and corresponding sulfur dioxide values excluded, the data transformations are once again applied. The results of Bartlett's test on the three forms of the data are shown below for each variable.

(1) SO_2

The test statistics and significance levels for the three forms of the data are shown in Table B.14. For both the run and collaborator-block data the linear transformation once again provides the best agreement. The estimates are obtained by pooling the sums of squares and degrees of freedom as shown in Appendix B 4. The run standard deviations and sample sizes are shown in Table B.15. Substituting these into the pooled variance formula gives:

Table B.14. SO_2 Data Transformation Summary, High Mist Values Excluded

Data	Transformation	Test Statistic	*df*	Significance Level
Run	Linear	1.624	13	1.000
	Logarithmic	2.763	13	0.999
	Square Root	1.655	13	1.000
Collaborator-Block	Linear	31.146	11	0.001
	Logarithmic	37.744	11	<0.001
	Square Root	34.028	11	<0.001

Table B.15. Sulfur Dioxide Run Summary, High Mist Values Excluded

Block	Run	Mean Concentration lb/scf x 10^{-7}	Standard Deviation lb/scf x 10^{-7}	Sample Size
1	4	324.50	53.66	4
	5	346.75	55.99	4
	10	408.00	71.25	3
2	1	479.50	37.48	2
	2	516.50	86.97	2
	3	333.67	88.82	3
	6	425.00	61.26	3
	7	489.00	76.02	3
3	8	457.50	71.30	4
	9	520.75	72.77	4
	11	511.00	77.54	3
	12	530.00	80.29	3
	13	475.00	82.37	4
	14	514.75	71.09	4

$$\delta_b^2 = \frac{\sum_{i=1}^{14}(n_i - 1)s_i^2}{\sum_{i=1}^{14} n_i - 14}$$

$$= \frac{163{,}577.25}{32}$$

$$= 5111.79.$$

The estimated standard deviation, then, is

$$\delta_b = \sqrt{5111.79}$$

$$= 71.50$$

with 3 degrees of freedom from the four labs. Using $\hat{\delta} = 448.67$, the sample mean of the 46 determinations, a coefficient of variation for between-laboratories is estimated as

$$\hat{\beta}_b = \frac{\delta_b}{\hat{\delta}}$$

$$= \frac{71.50}{448.67}$$

$$= 0.16$$

The within-laboratory pooled variance estimate is taken from the 12 collaborator-blocks estimates shown in Table B.16. This gives

$$\delta^2 = \frac{\sum_{i=1}^{12}(n_i - 1)s_i^2}{\sum_{i=1}^{12} n_i - 12}$$

$$= \frac{147{,}948.37}{34}$$

$$= 4351.42$$

The within-laboratory standard deviation, then, is estimated by

$$\hat{\sigma} = \sqrt{4351.42}$$

$$= 65.97.$$

Table B.16. Sulfur Dioxide Collaborator-Block Summary, High Mist Values Excluded

Block	Collaborator	Mean Concentration, lb/scf x 10^{-7}	Standard Deviation lb/scf x 10^{-7}	Sample Size
1	Lab 101	383.00	74.32	3
	Lab 102	370.00	87.31	3
	Lab 103	322.00	21.93	3
	Lab 104	342.00	82.02	2
2	Lab 101	417.50	24.12	4
	Lab 102	529.00	49.50	2
	Lab 103	399.67	48.18	3
	Lab 104	452.00	150.86	4
3	Lab 101	464.50	24.83	4
	Lab 102	582.00	15.13	6
	Lab 103	436.00	18.94	6
	Lab 104	504.83	80.08	6

There are 34 degrees of freedom associated with this estimate. The estimated coefficient of variation is

$$\hat{\beta} = \frac{\hat{\sigma}}{\hat{\delta}}$$

$$= \frac{65.97}{448.67}$$

$$= 0.15$$

The laboratory bias variance is estimated from the between- and within-laboratory components as

$$\hat{\sigma}_L^2 = \hat{\sigma}_b^2 - \hat{\sigma}^2$$

$$= 5111.79 - 4351.42$$

$$= 760.37.$$

This gives an estimated laboratory bias standard deviation of

$$\hat{\sigma}_L = \sqrt{760.37}$$

$$= 27.57,$$

and a coefficient of variation estimate of

$$\hat{\beta}_L = \frac{27.57}{448.67}$$

$$= 0.06.$$

(2) H_2SO_4/SO_3

The data transformation results for the acid mist data excluding the 6 values above 60 lb/scf X 10^{-7} are given in Table B.17. The results correspond to those of the complete data set, with the logarithmic transformation

Table B.17. Acid Mist Collaborator-Block Summary, High Values Excluded (lb/scf × 10 $^{-7}$)

Data	Transformation	Test Statistic	*df*	Significance Level
Run	Linear	27.850	13	0.009
	Logarithmic	12.139	13	0.516
	Square Root	18.192	13	0.150
Collaborator-Block	Linear	35.417	3	0.000
	Logarithmic	15.338	3	0.002
	Square Root	23.219	3	0.000

the only acceptable one for the run data and the best for the collaborator-block data. Thus, a coefficient of variation approach is again used to obtain precision estimates for the acid mist data.

The estimated values for β_b and β are obtained by the technique of Appendices B.7 and B.8. The estimates obtained are linear combinations of the run and collaborator-block beta hats, weighted according to the number of observations used to obtain the estimates.

From the run data, the estimated between-laboratory coefficient of variation is

$$\hat{\beta}_b = \frac{1}{14}\sum_{i=1}^{14} w_i\hat{\beta}_i.$$

The beta estimates and their respective weights are given in Table B.18. Substituting into the above formula gives

$$\hat{\beta}_b = 0.661,$$

Table B.18. Acid Mist Run Summary, High Values Excluded

Run	Mean Concentration	Standard Deviation	Beta Hat	Weight
1	21.5	21.9	1.2778	0.481
2	21.2	15.1	0.8946	0.481
3	22.9	23.5	1.1577	0.890
4	19.5	19.1	1.0641	1.283
5	9.1	3.0	0.3567	1.283
6	9.1	4.5	0.5501	0.890
7	5.6	2.1	0.4232	0.890
8	12.9	6.3	0.5287	1.283
9	10.3	2.9	0.3110	1.283
10	10.2	2.7	0.3012	0.890
11	11.3	6.7	0.6720	0.890
12	13.6	10.7	0.8893	0.890
13	13.3	6.6	0.5384	1.283
14	10.7	8.2	0.8293	1.283

and an estimated standard deviation of

$$\hat{\sigma}_b = \hat{\beta}_b\delta$$

$$= (0.661)\delta.$$

There are 3 degrees of freedom associated with this estimate.

The four collaborator-block beta estimates and their weights shown in Table B.19 give an estimated within-laboratory coefficient of variation of

$$\hat{\beta} = \frac{1}{4}\sum_{i=1}^{4} w_i\hat{\beta}_i$$

$$= 0.585.$$

The within-laboratory standard deviation is estimated by

$$\hat{\sigma} = \hat{\beta}\delta$$

$$= (0.585)\delta$$

with 42 degrees of freedom.

Table B.19. Acid Mist Collaborator-Block Summary, High Values Excluded (lb/scf × 10^{-9})

Block	Collaborator	Mean Concentration	Standard Deviation	Beta Hat	Weight
1	Lab 101	18.12	16.97	0.9602	0.954
	Lab 102	6.98	1.69	0.2484	0.954
	Lab 103	13.60	7.28	0.5474	1.046
	Lab 104	13.94	7.98	0.5857	1.046

The laboratory bias component is estimated from the above. The estimated laboratory bias coefficient of variation is

$$\hat{\beta}_L = \sqrt{\hat{\beta}_b^2 - \hat{\beta}^2}$$

$$= \sqrt{(0.661)^2 - (0.585)^2}$$

$$= \sqrt{0.095}$$

$$= 0.308.$$

The laboratory bias standard deviation, then, is estimated as

$$\delta_L = \hat{\beta}_L \delta$$

$$= (0.308)\delta.$$

B.11 The Unknown Sulfate Solution Test Data

An unknown sulfate solution test was conducted as part of the Method 8 collaborative study to isolate the precision and the accuracy of the analytical phase of Method 8. 10-mℓ samples of three sulfate solutions, labeled Solution A, Solution B, and Solution C, in which the prepared sulfate concentrations were unknown to the collaborative laboratory teams, were analyzed in triplicate on each of three days by each team in conjunction with its collaborative test samples. Figure 4 in the main report shows the instruction and reporting form.

The corrected sulfate solution concentration data are presented in Table B.20. Lab 101 introduced a 0.71 percent error into its sulfur dioxide concentration calculation on four of its aliquots by incorrectly copying its barium perchlorate titrant normality determination. The error has been corrected in the Table B.20 data. Table B.21 is a summary of the Table B.20 data averaged over replicates and days to show the collaborator (laboratory bias) effect. Whereas Labs 101, 102, and 103 obtained reasonably accurate sulfur dioxide determinations using Method 8, Table B.21 shows that Lab 104's determinations fell 6 to 9 percent below the true values. Table B.20 affirms the consistency of this Lab 104 negative bias.

B.12 Analysis of Variance in the Unknown Sulfate Solution Test

A separate analysis of variance was performed on the Table B.20 data reported for each unknown solution. The factors in each analysis of variance consist of a collaborator factor, C, a day factor, $D(C)$, nested within C, and a replicate factor, $R(CD)$, nested within days within collaborators. Based on a random effects model, the analysis of variance, the variance components, and their significance levels are tabulated as Table B.22 for each of the three unknown solutions. The collaborator factor C is a very significant effect ($\hat{\alpha} < 0.001$) at every solution concentration. The size of the collaborator effect results, as Appendix B.11 discussed, from the consistently 6 to 9 percent low Lab 104 determinations. The day factor $D(C)$ is only significant at the high Solution B concentration.

The precision of the Method 8 analytical phase can be estimated from the Table B.22 analysis of variance. The collaborator factor C corresponds to the laboratory bias precision component of the main report. Since the Method 8 runs comprising a collaborator block were generally analyzed on different days in the laboratory, the day factor D is a within-laboratory effect. So the day and replication factors together correspond to the within-laboratory precision component of the main report. Thus, the Method 8 analytical phase variance components at each unknown solution concentration are estimated as $s_L^2 = \hat{\sigma}_C^2$ for laboratory bias, $s^2 = \hat{\sigma}_D^2 + \hat{\sigma}_R^2$ for within-laboratory, and $s_b^2 = \hat{\sigma}_C^2 + \hat{\sigma}_D^2 + \hat{\sigma}_R^2$

Table B.20. Corrected Sulfate Solution Concentrations, 10^{-9} lb SO_3/scf

Unknown Solution	Day	Replicate	Collaborator			
			Lab 101	Lab 102	Lab 103	Lab 104
A	1	1	423	415	419	385
		2	423	412	417	387
		3	419	414	417	387
	2	1	422	415	417	387
		2	422	414	416	387
		3	425	415	416	386
	3	1	424	414	416	387
		2	424	412	417	386
		3	424	415	416	387
B	1	1	672	656	664	621
		2	672	658	662	620
		3	670	656	663	622
	2	1	673	658	668	622
		2	673	656	669	622
		3	673	658	668	621
	3	1	669*	658	663	620
		2	665	658	663	621
		3	673*	656	663	621
C	1	1	158	159	159	149
		2	163	160	159	149
		3	166	160	159	149
	2	1	156	160	159	149
		2	159	160	158	149
		3	158	159	158	149
	3	1	173*	160	158	148
		2	158	160	158	148
		3	158	159	157	149

*Reported concentration adjusted upward by 0.71 percent to correct for normality calculation error.

Table B.21. Average Laboratory Sulfate Solution Concentrations, 10^{-9} lb SO_3/scf

Unknown Solution	Prepared SO_2 Concentration	Collaborator			
		Lab 101	Lab 102	Lab 103	Lab 104
A	423.0	422.9	414.0	416.8	386.6
B	669.8	671.1	657.1	664.8	621.1
C	158.6	161.0	159.7	158.3	148.8

Table B.22. Analysis of Variance of Sulfate Solution Data by Concentration

Factor	Sum of Squares	D.F.	Mean Square	Expected Mean Square	Variance Component	F-Ratio	Significance, $\hat{\alpha}$
Solution C, Mean = 156.9 X 10^{-7} lb/scf							
C	832.33	3	277.44	$9\sigma_C^2 + 3\sigma_D^2 + \sigma_R^2$	$\hat{\sigma}_C^2 = 29.94$	34.81	<0.001
D(C)	54.22	8	6.78	$3\sigma_D^2 + \sigma_R^2$	$\hat{\sigma}_D^2 = 0$	0.85	>0.50
R(CD)	191.33	24	7.97	σ_R^2	$\hat{\sigma}_R^2 = 7.97$		
Solution A, Mean = 410.1 X 10^{-7} lb/scf							
C	6999.22	3	2333.07	$9\sigma_C^2 + 3\sigma_D^2 + \sigma_R^2$	$\hat{\sigma}_C^2 = 259.04$	1333.18	<<0.001
D(C)	14.00	8	1.75	$3\sigma_D^2 + \sigma_R^2$	$\hat{\sigma}_D^2 = 0.10$	1.22	≈0.40
R(CD)	34.67	24	1.44	σ_R^2	$\hat{\sigma}_R^2 = 1.44$		
Solution B, Mean = 653.5 X 10^{-7} lb/scf							
C	13494.75	3	4498.25	$9\sigma_C^2 + 3\sigma_D^2 + \sigma_R^2$	$\hat{\sigma}_C^2 = 498.65$	430.87	<<0.001
D(C)	83.56	8	10.44	$3\sigma_D^2 + \sigma_R^2$	$\hat{\sigma}_D^2 = 2.80$	5.14	0.001
R(CD)	48.67	24	2.03	σ_R^2	$\hat{\sigma}_R^2 = 2.03$		

Table B.23. Analytical Phase Precision Estimation

Unknown Solution	Mean, 10^{-7} lb/scf		Within-Laboratory		Laboratory Bias		Between-Laboratory	
	True, μ	Method 8, $\bar{x}$	Variance, $s^2 = \hat{\sigma}_D^2 + \hat{\sigma}_R^2$	Std. Dev., $s = \sqrt{\hat{\sigma}_D^2 + \hat{\sigma}_R^2}$	Std. Dev., $s = \hat{\sigma}_C$	Coef. of Var., $\hat{\beta}_L$	Std. Dev., $s_b = \sqrt{\hat{\sigma}_C^2 + \hat{\sigma}_D^2 + \hat{\sigma}_R^2}$	Coef. of Var., $\hat{\beta}_b$
C	158.6	156.9	7.97	2.82	5.47	0.0345	6.16	0.0388
A	423.0	410.1	1.54	1.24	16.09	0.0380	16.14	0.0382
B	669.8	653.5	4.83	2.20	22.33	0.0333	22.44	0.0335
			$\hat{\sigma}^2 = 4.78$	$\hat{\sigma} = 2.19 \times 10^{-7}$ lb/scf		$\hat{\beta}_L = 0.0353$		$\hat{\beta}_b = 0.0368$

for between-laboratory. The analytical phase precision estimates for each solution are developed and presented in Table B.23. Note that the within-laboratory standard deviation estimates are relatively constant, whereas the between-laboratory standard deviation estimates are proportional to the mean. On this basis, the Method 8 analytical phase within-laboratory precision was estimated in terms of the constant standard deviation $\hat{\sigma} = 2.19$ obtained by pooling the solution within-laboratory variance estimates. In contrast, the average between-laboratory coefficient of variation for the three solutions, $\hat{\sigma}_b = 0.0368$, was utilized as the Method 8 analytical phase between-laboratory estimate, using the technique of Appendices B.7 and B.8.

There were no instructions given to the collaborators regarding how to integrate the standard solution analyses with the stack sample analyses. In the case of Lab 101, one analyst prepared the samples for titration, and a second analyst performed the titration. The samples were assigned designations which did not indicate whether they were standard solutions or stack samples. As a result, the analyst performing the titration was unaware of which samples were the standard solutions and the estimated replication error from these data is truly an error term.

For the remaining labs, the analyst both prepared the samples and performed the titrations. Because of this, there was no way to prevent the analyst from knowing which were stack samples and which were standards. Also, the three replicates of the standard were probably run consecutively. Due to the difficulty inherent in determining the end point of the barium-thorin titration, the possibility exists that the volume of titrant required on the first sample influenced the volume used on the two subsequent repetitions.

To test this, an intraclass correlation coefficient [5] is calculated to determine if the errors, determined concentration minus true concentration, are related to one another. The class for this test is a single lab's repetitions of a given standard solution on the same day. Three coefficients are calculated, one for each solution, and these are shown in Table B.24. As can be seen, for each solution there is a strong correlation among the errors.

For comparison, a coefficient is calculated for Lab 101 alone, using the data from all three solutions, and this is also shown in Table B.24. This value is not significant, which indicates that the concentrations are indeed independent replicates.

The estimated σ_R^2 for each solution is calculated for each solution using the Lab 101 data alone, and these estimates are shown in Table B.25. It is apparent that these values are higher than those obtained from the full data set, and that the estimated variances in Table B.23 may have a low bias in them. If the Lab 101 estimates are in fact better estimates of the true replication error, the effect on the within-and between-laboratory standard deviation estimates would be relatively minor. The within-laboratory standard deviation would be larger by approximately 1 lb/scf $\times 10^{-7}$. The between-laboratory term is dominated by the laboratory bias term, which is unchanged, and the coefficient of variation would go from the present 3.68% to slightly over 4%.

Table B.24. Intraclass Correlation Coefficients

Source	r
Solution A	0.993
Solution B	0.995
Solution C	0.732
Lab 101, All solutions	0.022

Table B.25. Analytical Phase Replication Error, Lab 101

Solution	δ_R^2
A	2.78
B	5.78
C	31.22

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